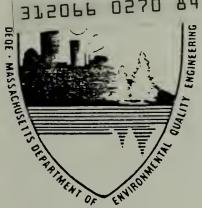
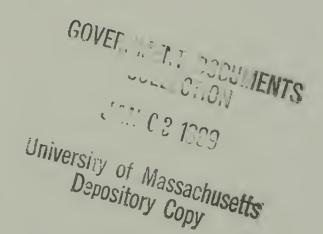
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COMMONWEALTH OF MASSACHUSETTS

DEPARTMENT OF ENVIRONMENTAL QUALITY ENGINEERING DIVISION OF WATER SUPPLY



HANDBOOK

OF

TREATMENT TECHNOLOGIES FOR

CONTAMINATED GROUNDWATER

December 1985

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HANDBOOK OF TREATMENT TECHNOLOGIES FOR CONTAMINATED GROUNDWATER

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The purpose of this handbook is to provide a concise summary of treatment technologies for groundwater and public water supply wells which have been contaminated with organic and certain inorganic compounds. An increasing number of municipalities in Massachusetts (approximately 70 as of June 1985) are discovering groundwater contaminants that pose real or potential threats to consumer health. In many cases it is often impossible to develop new sources of drinking water and therefore treatment becomes the only reasonable option. However, the presentation of this summary is not meant to mislead the reader into thinking that treatment is a routine, easy, and inexpensive process. It is not. Prevention of groundwater contamination remains the best and most cost effective course of action. Massachusetts cities and towns, as well as others across the nation, must become vigilant in their protection of our valuable and threatened water resource.

This handbook provides state, regional and local officials concerned with treating contaminated groundwater, as well as interested citizens, a starting point from which to understand and evaluate groundwater supply treatment proposals in terms of suitability, effectiveness and cost. It is hoped that this report will encourage critical and skeptical responses to simple or popular "one-option" approaches, and stimulate questions on other possible treatment options. It should be noted, however, that this summary can not replace the thorough site specific analysis necessary for a final decision.

The handbook is organized into three sections, two summary matrices and three appendices. Section I: Aquifer Restoration Decision Making outlines and briefly discusses the steps necessary to reach an effective strategy for a contaminated water supply. Section II: Treatment Technologies describes physical, chemical, surface biological and in situ treatment technologies in terms of the unit process, applications and limitations. Treatment systems are illustrated where necessary. Section III: Treatment Technology Cost Comparisons describes the factors that affect costs and provides useful cost comparisons of some of the technologies.

Two matrices and three appendices summarize and supplement the text. Matrix 1: Groundwater Treatment Alternatives versus Various Parameters essentially summarizes the technologies described in Section II. Matrix 2: Classes of Compounds versus Applicable Treatment Technologies matches some common organic contaminants found in groundwater with possible

treatment technologies. Appendix A lists organic compounds known to occur in groundwater nationwide. Appendix B lists the sources of groundwater contamination. Appendix C is a glossary of selected terms used in the text. References are provided to guide the reader to additional detailed information.

Those wishing an EXECUTIVE SUMMARY are directed to Matrices 1 and 2 and the following sections of text: Section I, Introduction p.1: Section II, Introduction p.6: Section III, Introduction p.64, Factors That Affect Costs p.65, and Cost Range Table p.76.

Recent national government surveys show that <u>volatile organic compounds (VOCs)</u>* are present in many public ground water supplies. VOCs are a general class of synthetic organic chemicals that include low-molecular weight volatile compounds. VOCs include halogenated(contain chlorine, fluorine, iodine, etc.) compounds. The three most commonly detected VOCs in groundwater supplies are <u>trichloroethylene(TCE)</u>, tetrachloroethylene(PCE) and <u>l.l.l trichloroethane(TCEa)</u>. These surveys also found that the concentrations of VOCs are often much higher in groundwater than in surface water supplies. Other widely encountered compounds include carbon tetrachloride, dichloroethanes, methylene chloride, benzenes and xylenes.

It should be noted that these studies focused on the detection of volatile organic compounds as opposed to non-volatile organic compounds. As analytical methods to detect non-volatiles are developed for use in future groundwater surveys, it is likely that the presence of many compounds from this class of organics will be discovered.

This handbook is meant to be a concise summary and this goal prevents the inclusion of voluminous detailed information. The reader is given references following each section for additional information. Some "state of the art" information is unavailable due to its proprietary nature. It has been recently learned that the U.S. Environmental Protection Agency and the New Jersey Department of Environmental Protection are developing summaries of treatment technologies. Both should be available by the end of 1986.

^{*} Terms underlined are defined in the Glossary, APPENDIX C

Introduction

Once contaminants are discovered in a groundwater supply, a decision must be made. This requires certain kinds of information and a great deal of study. The wrong decision (based on incomplete data or analysis) is costly, ineffective, and can sometimes make matters worse.

This section briefly discusses the principal steps that should be followed in order to develop an effective strategy for a contaminated water supply. Although brief mention is made of all the principal steps, this handbook discusses only treatment technologies (step 5) in detail. The reader is referred to the end of this section for several useful publications dealing with the other aspects of the decision process.

The steps discussed in this section are :

- 1. Characterize contamination
- 2. Define hydrogeology
- 3. Define, investigate options; Choose course of action
- 4. Formulate cleanup objectives if cleanup is chosen
- 5. Identify feasible technologies
- 6. Do feasibility studies on selected treatment technologies
- 7. Select treatment method(s)
 - a. Do pilot studies
 - b. Start full scale operation
- 8. Initiate monitoring program

Additional steps may be required in certain cases in order to be in compliance with Federal or State clean-up legislation. For example, in Massachusetts, there are as yet no specific guidelines on restoring contaminated municipal groundwater supplies: Decisions are made on a site by site basis. However, if a site is being cleaned up under CERCLA (Superfund), there are two documents (USEPA, 1985) that provide guidance for the preparation of feasibility studies and remedial investigations. A recommended report format is provided in these documents and the specific elements to be included are described.

Restoration Decision-Making Steps:

1. Characterize Contamination

To assess the magnitude of the problem, a thorough characterization of the contamination is necessary. This study should determine:

1. What contaminants are present and in what amount?

- 2. How widespread is the problem- other wells? other aquifers?
- 3. The potential source(s) of the contamination and probable extent of the plume
- 4. Health risks

2. Define Hydrogeology

Competent and well-focused hydrogeologic studies are essential. They are the basis for the development of a model of the groundwater flow in the area. A thorough understanding of the subsurface system is necessary in order to characterize the contaminant plume and evaluate the options available.

3. Define and Investigate Options; Choose Course of Action

After contaminant and hydrogeologic information is obtained, the next step is to decide what if any action is to be taken. Listed below are some of the general options available. Specific sites may have other options available to them. Also a combination of options can be chosen.

- o Abandon and properly seal the well
- o Abandon, seal the well and contain the contaminant source
- o Use shallow pumping techniques to avoid the contaminant plume moving below or through the lower portion of the aquifer
- o Manage the plume by means of pumping or injection methods to control the direction and migration of the plume
- o Pump and treat the water for recharge or use as a water supply
- o Use <u>in situ</u> treatment techniques

As demands for groundwater usage increase, the option to abandon a polluted aquifer is becoming limited. Also, even if a well is abandoned, treatment or containment is sometimes necessary to prevent pollution of other wells in the area.

4. Formulate Cleanup Objectives

If the decision is made to treat the groundwater, cleanup objectives must be formulated: Treat to recharge quality or to water supply quality. The objectives are determined by health, technical, environmental and economic factors.

Future needs and requirements as well as present ones need to be taken into consideration. For example, additional contaminants may arrive at the well head or Maximum Contaminant Levels (MCLs) may be revised downward.

5. Identify Feasible Technologies

Once a cleanup objective is determined, a treatment method is selected. The technologies available for remedial action fall into five broad catagories.:

- 1. Physical
- 2. Chemical
- 3. Biological
- 4. In-Situ (Physical, Chemical, Biological)
- 5. Point-of-Use

The specific alternatives in each category and their applications are listed in Matrix 1 and discussed in Section II.

6. Do Feasibility Studies

Feasibility studies should be done on all the possible treatment alternatives in terms of effectiveness of contaminant removal, cost, urgency and duration of treatment. Not all feasible technologies are appropriate to a particular site. For example, some biological alternatives that can achieve the contaminant removal objectives and are cost effective, take a considerable amount of time and therefore are not practical in urgent situations.

7. Select Treatment Method(s)

Once a treatment method or combination of methods is chosen, pilot studies should be carried out. The importance of these studies can not be overemphasized. Theoretical and laboratory data often fall far short of reality. In addition, full scale operational data is limited and difficult to extrapolate because treatments are so site-specific. The pilot studies must be adequate (i.e. aeration towers that are tall enough and carbon runs that are long enough) in order to obtain reliable data. Otherwise, a viable treatment alternative might be eliminated or an incorrect one chosen that does not hold up to long term full-scale operation.

After the pilot studies are completed, professionally evaluated and accepted, a full scale facility should be designed. It is important to work closely with local and state officials during the permit and construction phase of these projects.

8. Initiate Monitoring Program

A maintenance and monitoring program is the final step. The complexity of the program depends on the chosen treatment technology. For example, the monitoring program for a carbon adsorption facility is much more complex than one designed for a tower aeration facility.

Aquifer restoration planning is a complex mix of scientific, engineering, health, economic, community and political factors. The objectives are not achieved overnight. For example, although contamination was first discovered in the water supply for Provincetown, Massachusetts in 1977, the full scale treatment facility did not start operation until May 1985.

Cleanup projects can be finite (5-10 yrs) or permanent depending on whether or not the source of contamination has been closed, and upon the nature and volume of the contaminants.

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SECTION II: TREATMENT TECHNOLOGIES

Introduction

In this section, treatment technologies are divided into five groups:

- A. Physical
- B. Chemical
- C. Surface Biological
- D. <u>In-Situ</u> (physical, chemical, biological)
- E. Point-of-Use (home treatment)
- A. Physical treatment methods remove contaminants by phase or component separation. Phase separation is fairly straightforward and includes skimming and conventional filtering techniques to remove any immiscible or solid phase(s). In component separation, actual ionic or molecular components are removed from the water using processes such as adsorption, stripping and reverse osmosis. The types of physical treatment technologies that will be discussed in Section II are:
 - 1. stripping
 - 2. adsorption
 - 3. filtration
 - 4. reverse osmosis
 - 5. skimming
- B. Chemical treatment methods change the chemistry of the water allowing removal of specific types of compounds. The transformations can be achieved through neutralization, precipitation or oxidation. Common applications include removal of metals and neutralization of corrosive components. The types of chemical treatment technologies that will be discussed in Section II are:
 - 1. Coagulation/Clarification
 - 2. Ion Exchange
 - 3. Chemical Transformation
 - a. chemical oxidation
 - b. chemical reduction
 - c. pH adjustment
- C. Surface Biological treatment methods use native or introduced bacterial populations to convert toxic contaminants to non-toxic by products in above ground treatment systems. The types of biological treatment technologies that will be discussed in Section II are:
 - 1. Aerobic (activated sludge, aeration lagoons) digestion
 - 2. Anaerobic digestion.

- D. <u>In-Situ</u> techniques immobilize or detoxify contaminants in place in the aquifer. The types of <u>in-situ</u> treatment technologies that will be discussed in Section II are:
 - 1. Physical Adjustments
 - 2. Chemical Degradation
 - 3. Biological Degradation
- E. Point-of-Use treatment systems treat water directly in the home (or institution) and are generally used by owners of private wells. Technologies currently available for point-of-use treatment and discussed in this section are:
 - 1.adsorption with activated carbon
 - 2.air stripping

Many of these technologies have been available to the wastewater and waste treatment industries for some time. They are now being rapidly adapted for water supply treatment. Presently, some other methods such as incineration (of water or soil) and soil removal have limited use for treatment of contaminated groundwater. However, since groundwater treatment is a relatively new industry, many advances can be expected in the near future.

II A.1. AIR STRIPPING .

Introduction

Air stripping is a process whereby a substance dissolved in water becomes dissolved in air. Stripping is an effective treatment method for removing volatile organic compounds (VOCs) from groundwater because VOCs dissolved in water naturally diffuse into available air.

The transfer of a contaminant from the liquid phase to the gaseous phase is accomplished by injecting air into the contaminated water using various aeration designs and techniques. Some of these designs and processes are described below.

II.A.1.a. AIR STRIPPING

Aeration Designs

The commonly used aeration designs for air stripping are diffused aeration, induced draft, and tower aeration.

Diffused aeration

In diffused aeration, stripping is accomplished by bubbling air into a contact chamber filled with water to be treated. The untreated water enters the top, treated water exits the bottom while air runs counter current (Figure 2.1). Specific factors that affect removal efficiencies for this design are water depth and bubble size.

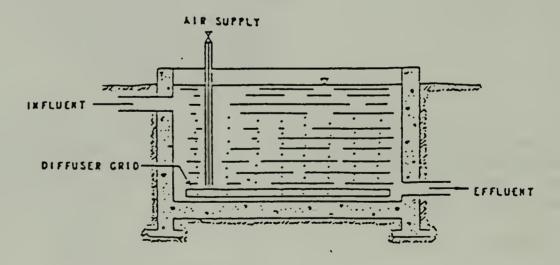


Figure 2-1. DIFFUSED AIR BASIN

(Dyksen et al.,1982) Reprinted from AWWA, 1982 Annual Conference Proceedings, by permission. Copyright @ 1982, The American Water Works Association.

Pilot studies at Peace River, Fla. and Glen Cove, N.Y. indicate removal of 50-90% of several VOCs (Singley, 1982, Ruggiers and Feige, 1984). This stripping technique is generally less effective and more expensive than the packed tower technique (Dyksen et al. 1982). However, diffused aeration is an effective system when it is necessary to dissolve a gas in the water (i.e. ozonation or oxygenation, p. 29) as part of the treatment process (Dyksen, 1982).

Induced-Draft

The induced-draft stripper design provides air/water contact without using blowers or packing material. Water enters one end of the chamber through spray nozzles which induce air to enter the stripper chamber. (Figure 2.2). Calgon Corporation (Emerson, no date) claims to reach removal efficiencies of 60-85% for VOCs and suggests this design for use in combination with carbon adsorption. IT SHOULD BE NOTED THAT 90% (OR EVEN 99%) REMOVAL MAY STILL NOT RENDER THE WATER POTABLE SINCE THE INITIAL INFLUENT CONCENTRATION AFFECTS THE FINAL EFFLUENT CONCENTRATION.

Tower Aeration

Tower aeration designs include packed towers, wood slat trays, coke trays and others. The most common and most effective of these is the packed tower or column (Dyksen et al., 1982).

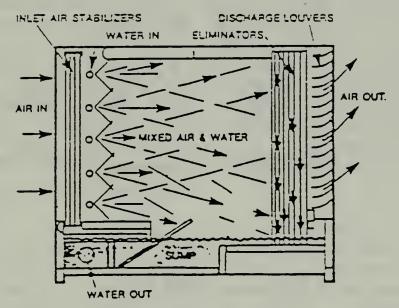


Figure 2-2. Pllot Induced-draft stripper.

(O'Brien and Stenzel, 1984) Reprinted by permission.

In a packed tower air stripping system, water to be treated percolates through an inert packing material (designed for maximum air/water contact) while air is forced up from the bottom (Figure 2.3). Depths of packed beds range from 4 to 33 feet and overall tower heights range from 12 to 50 feet (Lenzo, per. comm. Nov.1985). The treated water exits from the bottom of the tower for direct use or recharge while the volatile component exits with the air (off-gas) from the top of the tower for either discharge into the atmosphere or treatment. Using this technique, it is important to assure that discharged off-gas is not incorporated into the intake air since this will lower removal efficiencies (Singley, 1982). Treatment of the off-gas is generally accomplished via fume incinerators or vapor phase carbon.

Whether the off-gas requires treatment depends on emission standards (these vary from state to state), and the nature and concentration of the compound in the off-gas. For example, TCE, PCE and 1,1,1 trichloroethane photo degrade in the atmosphere. TCE has a half-life of four hours in the atmosphere (APCA Journal, June 1983). Also, dispersion does take place so concentrations of compounds in the area of the tower are generally low.

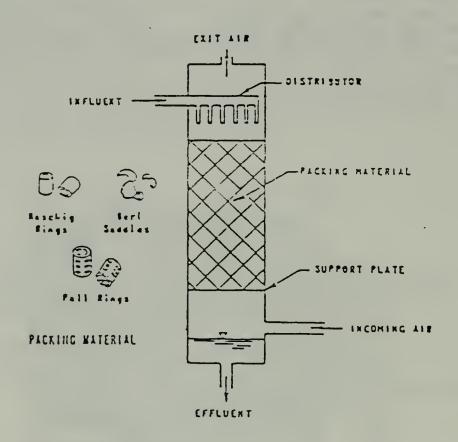


Figure 2-3. PACKED COLUMN

(Dyksen et al., 1982) Reprinted from AWWA, 1982 Annual Conference Proceedings, by permission. Copyright @ 1982, The American Water Works Association.

Unit Process

Generally speaking, the unit process of air stripping is theoretically capable of removing dissolved volatile organic compounds and some semi-volatiles. For any specific compound, solubility in water, boiling point and its Henry's Law constant, affect the ease of removal. As a general rule, VOCs with Henry's Law constants greater than 100⁻³ atm m³/mol are good candidates for air stripping. However, specific compounds need to be evaluated on an individual basis since constants below 100⁻³ atm m³/mol do not preclude treatment by aeration.

Factors that affect the removal efficiencies of any particular unit are: air/water ratios, flow rate, packing column height, temperature, influent water characteristics (pH, presence of metals etc.), the physical/chemical characteristics of the specific contaminant and removal requirements. Unlike efficiencies of removal by carbon adsorption, air stripping removal efficiencies are not effected by the presence of other solvents (Love et al 1983).

It is beyond the scope of this report to discuss specific design variations that maximize removal efficiencies, but a few general facts and principles are offered in order to assist in interpreting design proposals:

- o Increasing the air/water ratio increases the removal efficiencies. Ratios range from 10:1 to more than 500:1 (Canter and Knox, 1985).
 - o Slowing the flow rate (hydraulic loading) can increase efficiences and is often more effective and less expensive than increasing air/water ratios (Whittaker & Johnson, 1984, La Marre, per comm, 1985).
 - o Increasing the height of the packed bed increases the removal efficiencies since height determines, to a great extent, the available surface area for air/water interaction. The packing material for the towers comes in a variety of shapes and materials (Figure 2. 3). Pilot studies determine which packing is the most effective.

Groundwater temperature also affects removal efficiencies. For example, all design parameters being equal, removal efficiencies will be lower with 40° F groundwater than with 50° F groundwater. The average groundwater temperature in New England is 49° F (Geraghty et al, 1973). However, air temperature does not appreciably affect removal efficiencies

(Dyksen, 1982). When air temperatures are below freezing, equipment must be designed to prevent freezing of lines etc.

Characteristics of the water other than its VOC concentration can markedly affect the success of aeration treatment. For example, during air stripping, removal of/or treatment for high levels (above 4ppm) of iron and manganese (common metals in New England groundwater) may be necessary to prevent coating and clogging of packing materials with iron and manganese oxides (Stover & Kincannon, 1983). Also, pH adjustment is sometimes necessary to reduce the corrosive characteristics of certain water (below pH 4.5) that can adversely effect performance and durability of tower materials.

Applications and Limitations

Although simple aeration for the removal of tastes and odors from drinking water has been used in treatment plants since the last century (Baker, 1949), it has not always been a feasible removal treatment for VOCs. For example, incompatability between construction materials and corrosive water, and lack of field data have been two typical problems.

Today, advances such as injection molded plastic packing materials, the availability of field data and low operation and maintenance costs make air stripping an effective and economical treatment option for volatile organic compounds. An increasing number of companies are offering air stripping units. Portable towers similar to mobile adsorption units are also available.

The applications of air stripping are continually expanding as additional compounds need to be removed from groundwater. Some of the compounds considered amenable to air stripping are listed in Table 2.1.

Non-volatile compounds are not amenable to removal by air stripping. In general such compounds are more effectively removed by granulated activated carbon (GAC p. 16). However, when VOCs are present along with non-volatiles, a stripping unit is often used in combination with a GAC unit in order to prolong the life of the GAC bed.

TABLE 2.1

Selected Organic Compounds Amenable to Air Stripping

Vinyl Chloride
1,1 Dichloroethylene
cis-1,2, Dichloroethylene
trans-1,2 Dichloroethylene
trichloroethylene (TCE)
tetrachloroethylene (PCE)

Monochloroethane
1,1 Dichloroethane
1,2 Dichloroethane
1,1,1 Trichloroethane

Methylene Chloride Chloroform Bromodichloromethane Trichloroflouromethane Carbon Tetrachloride

Freon-113

Dlisopropylether t-Butylmethylether Benzene
Chlorobenzene
Ethylbenzene
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
1,2,3 Trichlorobenzene
1,2,4 Trichlorobenzene
Tetrachlorobenzene

Toluene Xylene

Acetone
Kethylethylketone (MEK)
Hethylisobutylketone (MIBK)

Isopropanol N-propanol 1-Butanol 2-Butanol

From Hydro Group, Product Literature Reprinted with permission

Detailed cost comparisons are discussed in Section III. However, in general, air stripping is a very cost-effective treatment process. Keep in mind that any design change that maximizes performance i.e. increasing column height, increasing air/water ratios, increasing temperature or treating "off-gas" also increases cost.

II A.1.b. STEAM (or HIGH TEMPERATURE AIR) STRIPPING

The processes of steam stripping are the same as in air stripping. Removal efficiencies are affected by the same factors. Simply stated, steam stripping is high temperature air stripping using a packed column stripping tower.

The purpose of steam stripping is to remove less volatile compounds by raising the process temperature to increase their volatility. The temperature of the system is raised by either running the contaminated water through a heat exchanger prior to loading on the column, or by heating the air that is forced up through the water. Temperatures range from $49-86^{\circ}\text{C}$ (120-180°F). Studies have shown that raising the water temperature is much more effective.

A concern with high temperature stripping is that the resulting higher water temperatures may make the water an unacceptable drinking source (D, D'Amore, per. comm. 1985). Consideration should be given to methods of dissipating the heat prior to distribution.

VOCs and semi-volatile or entractable organics with Henry's Law constants less than 10⁻³ atm m³/mol may be removed by steam stripping. Strier (1980) rates a compound as having good steam stripping capabilities if it has a boiling point (b.p.) of less than 150°C. However, new applications include removal of some phenols (b.p. 150°C) and chlorinated hydrocarbons (Stover and Kincannon, 1983).

Introduction

Adsorption is a physical process whereby molecules of a gas, liquid or a dissolved substance adhere to a surface. Adsorbent surfaces include naturally occurring adsorbents, activated carbon and synthetic resins (polymeric and carbonaceous adsorbents) (Isacoff and Bittner,1979). Activated carbon is the most widely used adsorbent in the water industry because it is such a broad spectrum adsorbent and is also very efficient in removing total organic carbon (TOC). Synthetic resins are used in wastewater treatment to remove and/or recover organic chemicals.

This section will describe the use of granular activated carbon (GAC) and synthetic resins (carbonaceous Ambersorb XE340) to remove organic contaminants of groundwater supplies.

II A.2.a. ACTIVATED CARBON ADSORPTION

Purification by means of carbon adsorption has a long history. Recorded use of carbon (in the form of charcoal) to purify water goes back to ancient Egyptian and Indian societies (Baker, 1949). However, it has only been during the last 40 years that activated carbon has gained wide-spread use for the removal of many organic compounds in a variety of industrial and municipal settings.

Unit Process

Activated carbon removes impurities from water by means of a physical process called adsorption. While water passes through the carbon granules, the organic pollutants are adsorbed from the water and held to the carbon surface by weak physical forces. This adsorption occurs because: a) the contaminant has a low affinity for water (low solubility) or b) the contaminant has a high affinity for the solid medium (carbon).

Carbon is able to trap and hold large amounts of organics because of its extensive internal pore structure. The tremendous surface area of the network of pores is produced by crushing and "heat activating" select grades of bituminous coal. One pound of activated carbon is said to equal the surface area of 100-150 farm acres (Calgon Corp,product literature). Activated carbon can be either powdered (PAC) or granular (GAC). In general, granular activated carbon is more commonly used for most water supply treatment applications.

A typical carbon adsorption treatment unit for a water supply consists of two or more vessels partially filled with a fixed bed of GAC (usually 20,000 lbs., a full truckload) (Figure 2.4). The vessels are commonly arranged in series to improve efficiency and monitoring.

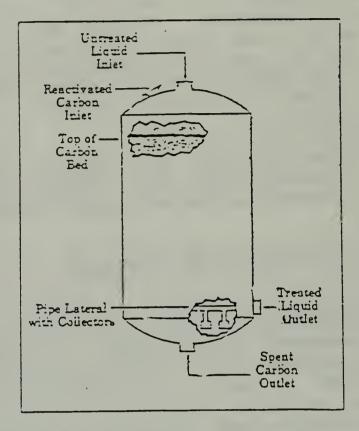


Figure 2-4. Carbon Adsorption Unit (Product Literature, Calgon Corp.) Reprinted by permission.

Applications and Limitations

Although GAC is able to remove a wide range of organic compounds (including VOCs), it is generally recognized that GAC is most effective in removing non-volatile organic conpounds. This ability combined with its extensive use in the water industry to treat odor and taste problems, make it a familiar and available technology to treat ground water contaminated with hazardous organic compounds.

The list of components adsorbable to GAC is long and includes many of the common low molecular weight groundwater contaminants. However, such removal often requires large amounts of carbon and frequent bed changes to prevent breakthrough of contaminants. Such requirements are often impractical and too expensive.

Also, low molecular weight compounds (that are weakly adsorbed), desorb in the presence of a more strongly adsorbed compound. This "competitive adsorption" is a problem since contaminated groundwater usually contains more than one compound.

Since other processes have been refined and developed for groundwater treatment the pressure for GAC to be the only answer to groundwater contamination has eased. It is becoming increasingly clear that carbon is used to its best and most cost effective advantage when combined with other processes (O'Brien and Stenzel,1984). This extends bed life, saving the carbon for removal of contaminants in the water not amenable to other treatment methods. In general, compounds that are most amenable to GAC adsorption have some or all of the following chemical characteristics: low water solubility, high molecular weight, low polarity, unsaturated carbon bonds (-C=C-), and aromatic structure (contains at least one benzene ring) (Strier, 1980)

Some compounds that are amenable to removable by adsorption are listed below:

Methylene chloride
Dichlorobenzenes
Polychlorinated biphenyls
Xylenes
n-Hexane
Methyl ethyl ketone

1,2 dichloroethane ethylene glycol chlordane kerosene formaldehyde pesticides

Factors That Affect GAC Performance

The effectiveness of carbon adsorption is influenced by a number of factors. These include:

- 1. design parameters
- 2. quality of influent water (pH, temperature, presence of metals or other non-toxic organics).
- 3. preparation method of activated carbon
- 4. nature and concentration of contaminants

1. Design Parameters

One of the most critical design parameters for any adsorption system is contact time. This is the length of time the contaminated water is in contact with the carbon. Contact times can be increased by increasing carbon bed depth or decreasing the flow rate (gpm). A minimum of 12-15 minutes contact time is normally recommended for treatment of contaminated groundwater. To improve the efficiency of long contact times, two adsorber units can be connected in series (0'Brien and Fisher, 1983).

2. Quality of Influent Water

The quality of the influent water must be considered since it affects performance and carbon life:

- o The pH can affect adsorptive capacity. Organic acids adscrb better under acidic conditions.
- o Increasing the temperature decreases adsorption capacity although it may increase the rate of adsorption.
- The presence of metals such as iron and manganese can foul the carbon system and non toxic organics such as humic acid can compete for adsorption sites and cause the desorption of the target hazardous compounds (Canter, 1985). In some cases it is necessary to backwash the carbon to remove material that is clogging the pore spaces. This backwash water can become a hazardous waste requiring proper handling and disposal.

3. Production Methods

The raw materials and preparation method of GAC determine its capacity. Carbons with equal surface areas can exhibit different adsorptive characteristics depending on the activation procedure used (Calgon, product literature).

4. Contaminant Profile

The nature and concentration of the contaminants determine the effectiveness, design parameters and cost of any carbon adsorption unit.

Cost

All of the factors that affect the performance of GAC also affect the cost. The carbon itself is the major cost component of an adsorption system. Virgin carbon is used instead of regenerated carbon for treatment of potable water since changes in the adsorptive capacity can occur with successive regenerations (Stover, 1982). Therefore, saving money by regenerating carbon can not be done.

In general, GAC is an expensive treatment method and should be used to treat compounds not amenable to other less expensive methods. More information on costs is presented in Section III.

Types of resin

There are various synthetic resins (adsorbents) commercially available. The chemical nature of these resins can be quite different depending on their porosity, polarity, particle shape, surface area and <u>hydrophobic</u> surface characteristics (Dyksen and Hess, 1982).

Compared to activated carbon manufacture, there is much greater control over the chemical and surface characteristics during resin production. It is therefore possible to develop a given resin for a specific adsorption task.

One of the carbonaceous adsorbents (Ambersorb XE340, Rohm & Haas product*) was developed to remove low-molecular weight, non-polar organics. Although the resin has very little affinity for high-molecular-weight polar organics, its adsorbent capacity for low molecular weight organics per gram is much higher than that of activated carbon.

Pilot studies were conducted that compared the ability of granular activated carbon (GAC) and Ambersorb XE340 to remove chlorinated hydrocarbons found in a New Jersey well. The primary contaminants involved were 1,1,1 trichloroethane (512 $\mu g/L$) and tetrachloroethylene (195 $\mu g/L$). This study indicated that the resin could treat almost twice the volume of water than GAC could before breakthrough of 1,1,1 trichloroethane. The report went on to say that neither medium leaked any detectable tetrachloroethylene. In addition to its higher capacity, the resin required only a five minute contact time compared to 18 minutes for the GAC (Isacoff and bittner,1979). This was a very limited study (400 gallons of water tested) and may not reflect the long-term performance of resin.

The USEPA funded a three-phase study of a contaminated supply well in Glen Cove, N.Y. from 1979-1983 (USEPA,1984). Aeration and resin adsorption, both alone and in combination, were evaluated for their ability to remove several common VOCs (TCE,PCE etc.). Capital and operation costs were also estimated for full scale installation.

^{*} Mention of a product or manufacturer does not imply endorsement by Massachusetts Department of Environmental Quality Engineering or the USEPA.

Test results using Ambersorb XE340 showed this resincapable of reducing contaminant levels to less than l $\mu g/L$. It was also demonstrated that the resincould be steam regenerated on site with more than 90% of virgin adsorbent capacity regained. However, further development of condensate separation and handling was thought to be necessary.

In 1983, the manufacturer of the resin (Rohm & Haas) announced that Ambersorb XE340 would not be produced commercially and its future as a groundwater remediation tool was left in doubt.

Unit Process

The operation of a resin adsorption system is similar to one for carbon with two or more tanks in series. Once a specific resin is selected, the effectiveness would be influenced by contact time, nature and concentration of contaminants, and the quality of the influent water (see page 18).

Applications and Limitations

Since Ambersorb XE340 is not commercially available and limited performance data have been published, it is difficult to assess the potential applications and limitations of this material. In general, this resin in laboratory studies is very effective in removing volatile, nonpolar compounds that are not well adsorbed by GAC. Also, it may be able to achieve (in general) lower effluent levels than with GAC (Flor, Rohm & Haas, per comm. July,1985). This is an important criteria when treating drinking water supplies.

Other commercially available resins are most useful in standard waste water treatment where the water quality is well defined and consistant (Pojasek, per comm. June, 1985).

Resin systems often need a pretreatment sand filter because resin is more subject to fouling by humic acids compared to carbon. Also, competitive adsorption is a problem (Pojasek, per. comm. June, 1985).

The major limitations of resin adsorption techniques are a lack of field knowledge specific to groundwater treatment, and high cost.

Cost

More field experience is needed to better estimate the cost of resin adsorption for treating contaminated groundwater supplies. As of 1982, cost for the resin was approximately \$10 per pound compared with \$0.65 per pound for GAC. However, this high material cost may be offset by other capital and O&M

factors. Dyksen & Hess (1982) point out that resins may be more cost effective than other treatment technologies in specific cases because of smaller contact tanks, shorter contact time, lower regeneration cost (using on-site steam regeneration), and higher adsorption capacity per pound of adsorbent compared to GAC.

Recent Developments

Commercial production was stopped on Ambersorb XE340 a few years ago. However, it has been recently learned that Ambersorb XE340 may be available in 1986 for research treatment purposes and some analytical procedures (Flor, per. comm., July, 1985).

Field evaluations are planned to compare this resin's capacity and its ability to achieve lower effluent levels than those of GAC. Also, studies will compare resin adsorption to air stripping. Depending on the results of these field tests, Ambersorb XE340 may be commercially available by 1988.

Introduction

Filtration is the process of passing a liquid through a porous medium in order to remove suspended particulate matter.

Unit Process

Filtration was first used centuries ago to purify water (Baker,1949) and is still a common process in conventional water treatment facilities. The most common filtration system utilizes sand, or sand with gravel, as a filter medium to remove suspended matter such as silt, clay, colloids and some microorganisms (Baylis,1971). The filter bed is contained within a basin or tank which allows the filtered liquid to be drawn off.

Applications and Limitations

Full scale conventional water treatment plants are unable to remove tetrachloroethylene, 1,2-dichloroethane or carbon tetrachloride by coagulation, sedimentation and filtration (Love and Eilers,1982). These authors assume that other VOCs would also not be effectively controlled by such conventional water treatment methods.

Although filtration does not directly remove VOCs, it is recognized as an important intermediate process when treating certain groundwater contaminated with hazardous organic compounds. For example, it is used to remove naturally occurring suspended solids and residual floc (wooly appearing precipitate produced by chemical precipitation) which would clog adsorption or stripping systems that are designed to remove VOCs in subsequent treatment processes (Stover and Kincannon, 1983).

Introduction

Reverse Osmosis (RO) is an osmotic filtration process that separates dissolved inorganic and organic material (solute) from a solvent (i.e. water).

Unit Process

This filtration is done by using a membrane more permeable to water than to the solute and by applying pressure (up to 1500psi) that exceeds the osmotic pressure of the solution. The pressure causes a solvent (water) flux through the membrane in a direction opposite to the normal osmotic flow, leaving the contaminant behind.

Application and Limitations

Inorganics

RO can effectively remove 80-97% of a wide range of inorganics (sodium, chloride, calcium, magnesium, sulfate, etc.) found in groundwater but the high cost of this technology has limited its use (Sorg and Love, 1984). It has been used for many years in Florida to produce potable water from brackish or saline water and to recover metals from wastewater (e.g. silver recovery).

Non-Volatiles

In the early seventies, reverse osmosis was considered a promising technique for the removal of persistent non-volatile high molecular weight compounds. Edwards and Schubert (1974) studied 2,4-D removal by RO but the results were variable (1-65% retentation). Other studies mentioned gave varying and sometimes contradictory results for Lindane and DDT retention.

Edwards and Schubert suggested that RO might best be used as a technique to prepare water samples for pesticide analysis rather than as a treatment technique.

Volatiles

The same authors mentioned that RO achieved partial removal of low to intermediate molecular weight organics but considered such removal a secondary technique.

Recently, the USEPA decided to conduct RO treatment studies on VOCs commonly found in groundwater (Sorg and Love,1984). Initial short duration (1-4hrs) laboratory results were encouraging but follow-up studies revealed that certain compounds (TCE, benzene, EDB and others) permeated the membrane within a few hours. RO removed 98% of the carbon tetrachloride and 1,1,1 trichloroethane throughout the test period but the tests were conducted for only 21 hours.

Future Use

While RO treatment is promising for some pollutants, it is not economically feasible at this time. Even when used in the most appropriate setting (desalination) there are many operating and maintenance problems. The average total cost of existing RO water treatment plants is \$2.76/1000 gal (Eisenberg and Middlebrooks,1984). This high cost and the availability of other proven effective and less expensive technologies preclude the general use of this alternative. However, it may be the treatment of choice in very specific cases. For example, if a specific amenable organic contaminant is discovered at a site that has an existing desalination RO plant, modification of that plant might be the best treatment solution.

Introduction

Skimming is the physical removal of floating contaminants (oil, grease, gasoline, and other light hydrocarbons) from a multi-layer solution. The process of removing floating hydrocarbons (free product) can take place directly in a well or at an above ground collection system. Since this process is the initial step in treating leaks from underground storage tanks (a common source of groundwater contamination) free product recovery alternatives are discussed in some detail.

Unit Process

Various systems are available to recover floating hydrocarbons. These include infiltration trenches, skimmer systems, oil/water surface separation and one- or two-pump recovery systems. Specific site conditions determine the choice of removal method.

Trench systems (Figure 2.5) can be used to contain and then recover limited spills at a site with a shallow groundwater table. A skimmer system or single pump unit is used to remove the floating product (along with some water) which is then separated in an above ground oil/water separator. Although the skimmer system draws up less water than the trench system, the rate of recovery is slow. This can add to the cost of the project and possibly allow the hydrocarbons to migrate and become dissolved in the groundwater. Pumped trenches, by creating a gradient toward the trench, recover the free product more rapidly. However, more rater is mixed with the floating hydrocarbons during removal and this larger volume (containing higher concentrations of dis lved hydrocarbons due to mixing) must be treated before discharge.

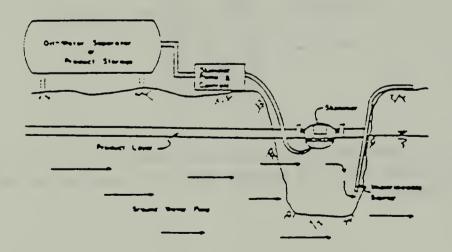


Figure 2-5. Open interceptor trench utilizing a Skimmer Pump

(Blake and Lewis, 1982) Reprinted by permission of Water Well Journal Publishing Co. @ 1982. All rights reserved.

Single pump recovery systems are another option for free product recovery. They have the advantage of being cheaper than two-pump systems because smaller diameter wells can be used, and complicated electronic controls are not required. However, this system requires separators to recover the product at the surface. Agitation of the free product during pumping may make subsequent separation difficult and result in higher concentrations of dissolved hydrocarbons in the wastewater (Blake and Lewis, 1982).

The most popular and efficient system is the two-pump recovery system (Figure 2.6). This system uses one pump (the water pump) to create a cone of depression in the water table which then causes the floating free product to flow toward the product recovery pump.

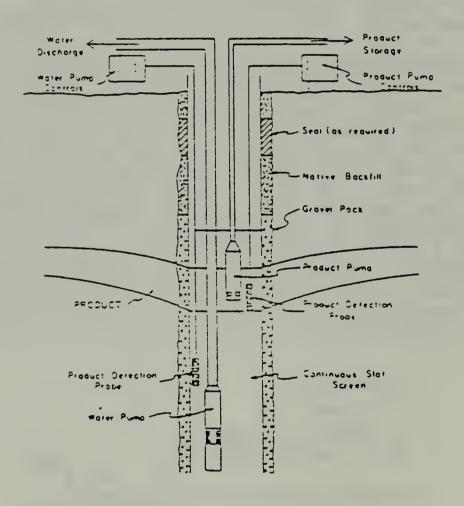


Figure 2-6. Two-pump Skimming Recovery System (Blake and Lewis, 1982) Reprinted by permission of National Water Well Association @1982. All rights reserved.

Since the free product is separated from the water in the well, surface oil/water separators are not usually required. Also, this system minimizes the amount of soluble hydrocarbons dissolved in the wastewater. However, a larger diameter well is required to house both pumps and the complicated, more expensive electronic monitoring equipment requires frequent inspections by trained personnel. These factors that add to the cost of recovery are frequently offset by the savings due to efficiency and speed of recovery. A discussion of skimming costs can be found in Section III.

Applications and Limitations

Some form of skimming to remove and recover free product is commonly the first phase of cleaning up a gasoline (or jet fuel etc.) spill or underground storage tank leak. Site conditions must be thoroughly understood in order to install the most efficient and speedy recovery system. The proper system, quickly installed, can minimize migration of the hydrocarbons and subsequent adsorption and/or solubilization of hydrocarbon components.

Skimming can not remove the petroleum products adsorbed to the soil or dissolved in the groundwater. It is estimated that only 30-60% of a hydrocarbon spill is recoverable as free product (see page 45). The treatment of adsorbed or dissolved gasoline components is the second phase of a hydrocarbon cleanup and can include one or more of the following techniques: biological treatment (<u>in situ</u> and/or surface), air stripping, carbon adsorption, soil removal.

Introduction

Conventional water treatment plants use various chemical processes to improve water quality. Hazardous waste streams are also treated by some of these methods to detoxify or remove various compounds.

Although, in general, these technologies do not adequately remove hazardous organic compounds from water supplies, certain processes are effective for removing many toxic inorganic compounds and selected organics or for pretreating water for organics removal. This section will describe coagulation/clarification, ion exchange, and chemical transformations by means of chemical oxidation, reduction and pH adjustment.

II B.1. COAGULATION/CLARIFICATION

This process removes colloidal solids, heavy metals and other compounds by the addition of coagulants such as lime, alum (a double sulfate of ammonium) and various polymers. The coagulated particles formed are than removed from the water by sedimentation or filtration.

Iron and manganese removal from groundwater by lime addition has been reported as a pretreatment step when followed by pH adjustment and air/steam stripping (Stover and Kincannon, 1983).

II B.2. ION EXCHANGE

Ion exchange removes selected ions from water and replaces them with ions from an insoluble solid salt (ion exchanger). The process can theoretically remove both organic and inorganic ions but because of technical constraints, most applications involve inorganic compounds (AWWA, 1971).

Barium and radium (found in some New England groundwater) have been removed from water using an ion exchange process (Myers et al.,1985). These laboratory studies indicated that removal requirements could be met with no other change in water quality. However, the authors point out that the process for this particular application needs refinement. Barium and radium can also be removed by lime softening a.d reverse osmosis.

Ion exchange is a proven method for nitrate removal. Although nitrate can also be removed from groundwater by reverse osmosis and electrodialysis(Sorg,1979), full scale operations have shown ion exchange to be the most efficient and economical treatment for nitrate removal (Sorg,1979; Lauch & Guter, 1985).

II B.3.a. CHEMICAL OXIDATION

In the treatment of hazardous wastes, oxidation is primarily used to convert compounds to less toxic forms or to carbon dioxide.

There are many oxidizing agents used. A few common ones are described here.

The ability of <u>ozone and ultraviolet light</u> to disinfect water supplies is well known (AWWA,1971). Ozone is one of the most powerful oxidizing agents, sufficiently strong to break some carbon-carbon bonds. Ozonation has been used to treat some hazardous wastes. The USEPA funded a study of the combination of ozone and UV light for destroying hazardous waste (Edwards et al.,1982). It was found that this combined treatment approach could destroy PCBs, chlorodioxins, hydrazine, nitrobenzene and others.

Research is currently being carried out on ozonation of such compounds as dioxane. There is debate in the literature about just what byproducts are formed and whether they too are hazardous. Until this is resolved, ozonation has limited applications for groundwater remediation.

Ozonation combined with GAC was proposed as a means to prolonging carbon bed life and thus reduce the high cost of GAC adsorption for water supply treatment. A three year pilot study was conducted to evaluate the feasability and cost of this method to remove trace organic compounds and to reduce total organic carbon (TOC) (Neukrug et al.,1984). Breakthrough of VOCs occurred sooner on the ozone-GAC system than on the GAC only system. This was probably due to competition for the sites due to the low molecular weight compounds formed by the ozonation step.

Laboratory studies have been conducted to determine the effect of <u>ozonation on biodegradability</u> of toxic compounds that are refractory (resistant) (Medley and Stover,1983). Use of ozone could possibly not only increase biodegradation but also reduce compound levels that are too high (inhibitory). Three

resistant compounds were studied: acrylonitrile, 1.2-dichloropropane and 2,4 dinitrophenol. Results showed that omidation of acrylonitrile was not readily achieved and in fact showed adverse effects on biodegradation. Although 1,2 dichloropropane was not biodegradable, it was readily omidized at small ocone doses. The compound 2,4 dinitrophenol was not readily omidized, but ozonation increased its biodegradability. The authors point out that ozonation is probably not a broad spectrum chemical treatment but might be one effective and economical component of a treatment program in certain cases.

Hydrogen peroxide, potassium permanganate and potassium ferrate are other oxidizing agents used in treating wastewater that may be useful in aquifer remediation programs. In laboratory studies, potassium ferrate was reacted with a group of priority pollutants (DeLuca et al.,1983). Results showed that naphthalene and TCE were oxidized, but nitrobenzene was not. If conventional treatment facilities were already onsite, the use of ferrate as a pretreatment prior to carbon adsorption or air stripping might be practical in some cases. Field studies on chemical oxidation of hazardous VOCs and non-VOCs in terms of groundwater remediation need to be done before these hazardous waste treatment technologies can be practically considered for groundwater treatment.

II B.3.b. CHEMICAL REDUCTION

In addition to chemical oxidation, reduction is also used to convert hazardous waste compounds to less toxic forms. A reducing agent is used to lower the oxidation state (number of electrons that have been removed or added to an atom) of a hazardous substance. This chemical reduction can reduce the toxicity or change the chemical characteristics of the substance so that it can be handled more easily.

For example, chromium, a common contaminant of New England groundwater (due in part to the past extensive tanning industry) can be reduced by various reducing agents including sulfur dioxide and sodium metabisulfite. In the waste treatment industry, reduction is generally followed by chemical precipitation and sedimentation (USEPA, 1976).

Although chromium and other metals are common contaminants of New England groundwater, more study must by done to see if these waste treatment processes using chemical reduction can be successfully adapted to treat water supplies.

II B.3. c. pH ADJUSTMENT

Adjustment of the pH of the water to be treated is frequently a first step to subsequent chemical processes. It is also used to improve water quality for physical (GAC adsorption; air stripping) or biological treatment.

The proper pH is necessary to control the rate and direction of some chemical reactions (such as the subsequent precipitation or non-precipitation of dissolved iron and manganese), to make the water less corrosive or to meet requirements for biological systems. Some common chemicals used to adjust the pH are calcium carbonate, lime, sodium carbonate and hydrogen chloride (AWWA, 1971; Stover & Kincannon, 1983).

SECTION II C. SURFACE BIOLOGICAL TREATMENT AEROBIC and ANAEROBIC

Introduction

During surface biological treatment of contaminated groundwater, organic compounds are degraded by specific microorganisms by means of aerobic or anaerobic processes. The process selected may produce a carbon and energy source for the microbe, an intermediate unused product or in the case of anaerobic degradation--methane gas. This section will describe the processes of aerobic and anaerobic biodegradation and the two basic unit systems: suspended growth systems (activated sludge) and fixed film systems.

<u>Unit Systems</u>

The basic suspended growth system consists of a large basin into which contaminated water and air or oxygen (if aerobic) are introduced. The microorganisms are present as suspended material.

The fixed film systems provide an inert support for the microbes in the form of a stacked tower (Biological Tower) or rotating disc (Rotating Biological Contactor). The microorganisms form a slime layer on the support medium. As the water flows over the slime layer, contaminants are metabolized.

According to Canter(1985), both systems have the same removal efficiencies and both can be operated under either aerobic or anaerobic conditions. However, the fixed film system can be cheaper because it does not need aeration equipment and is easier to operate (Nyer and Sauer,1984). Absalon and Hockenbury (1983) add that fixed film systems do not have the settleability problems associated with suspended growth systems.

Aerobic vs. Anaerobic Biodegradation

Most of the studies of biodegradation of pollutants have focused on aerobic oxidative processes which degrade organic compounds to carbon dioxide and water. According to Kobayashi and Rittman (1982), this has been because aerobic processes are well known, relatively simple and commonly considered the most efficient and generally applicable. However, they go on to say that aerobic digestion requires the addition of oxygen and produces biological sludge which requires disposal.

Anaerobic processes that decompose organic matter to carbon dioxide and methane gas do not require aeration and produce relatively little sludge. They are generally considered slow, difficult to maintain and not well understood in aquatic

environments. Because of these reasons, few pilot studies have investigated their applicability to groundwater contamination. However, many important detoxifying reactions are known to occur in anaerobic systems (e.g. animal rumen) and these may prove to be a key first step in degrading otherwise resistant (refractory) organic compounds.

One of these reactions, for example, is reductive dechlorination (or dehalogenation). The attachment of chlorine is generally thought to make a compound resistant to biodegradation (Parsons and Lage, 1985). However, Newson (1985) reports that field and laboratory studies have shown that some halogenated aliphatics (compounds without a benzene ring structure such as TCE, trichloroethane and others) seem to be degradable by anaerobic (but not aerobic) processes.

Most of the biodegradation studies of either aerobic or anaerobic systems have used bacterial populations found in domestic sewage or sludge. However, other microbes including fungi, algae, molds, photosynthetic bacteria and actinomycetes are currently being investigated in laboratory environments (Kobayashi and Rittman, 1982). Although much more needs to be known about the mechanisms and requirements of these organisms, they show promise for application to resistant organic compounds.

Factors Affecting Feasibility and Efficiency

After determining that there is no biological inhibition in the contaminated groundwater, feasibility studies are done to see if the contaminants may be amenable to biodegradation. These studies are necessary because site specific characteristics and their interactions affect biodegradation. The following determinations are part of any assessment:

- 1. Presence of toxic metals such as arsenic, cadmium, or lead
- 2. Temperature
- 3. pH
- 4. Availability of nutrients such as nitrogen and phosphorous
- 5. Indigenous microbial populations that might be adapted to degrade contaminant(s) present
- 6. Presence of non-target organics that might compete for metabolites used by microbes
- 7. Concentration and physical/chemical characteristics of the contaminants and their possible degradation forms

Once the quality of the contaminated water is determined, steps can be taken to improve the biodegradation capability and rate. Pretreating the water can remove metals, adjust pH and add nutrients. Adapted microbes can be seeded in the water or

.

indigenous populations can be enhanced. Low temperatures slow the rate of biodegradation but New England winters do not preclude the use of this technique.

In addition, the physical/chemical characteristics of a pollutant (linear vs branched, attachment of certain chemical groups etc.) and its concentration greatly determine the feasibility of biological treatment. Compounds that are amenable to biotransformation under laboratory conditions may not be successfully transformed if the concentrations are either too low or too high. According to Wilson and McNabb (1983), concentrations above 100 mg/L are needed to support sufficient populations of adapted microbes. However, at high concentrations (1,000-10,000 mg/L) the compound may be only partially degraded due to depletion of nutrients and/or oxygen.

This minimum critical concentration range for organic contaminants which is often above the levels found in groundwater has been a major limiting factor. It is currently unknown whether a mixture of organics, each at low concentrations(a common characteristic of contaminated groundwater) might provide the minimum concentration needed by certain microbes. It has recently been learned that promising results have been attained using biological treatment to treat low levels of contaminants and to achieve acceptably low levels of pollutants in the effluent (Lenzo, 1985, per. comm.). More research in this area is necessary.

Applications and Limitations

Laboratory studies have shown that most of the <u>priority</u> <u>pollutants</u> are subject to some degree of biodegradation (Kobayashi and Rittman, 1982). Results under such strict conditions often do not carry over into field situations.

Most field applications of biodegradation have been limited to treating chemical spills and industrial wastewater. Under such conditions of high influent concentration many compounds have been shown to biodegrade. This group includes acrlyonitrile, several phenols, benzene, toluene, xylene, methylene chloride, ethylene glycol, other hydrocarbons and polynuclear aromatics (Cantor 1985, Flathman 1984, Absalon and Hockenbury 1983).

Use of biological degradation for treatment of groundwater is limited by the following factors:

- O Concentration of pollutants(s) is often below minimum critical concentration
- o Microbes are not always able to reduce contaminants to ppb levels required for direct use
- O Potential exists for formation of hazardous breakdown products due to incomplete biodegradation

•

However, recent laboratory and pilot plant results (Stover and Kincannon,1983) show that biological treatment of a contaminated groundwater may be feasible under certain circumstances. These studies found that a combination of pretreatment for metals, steam stripping and biologial treatment (rather than carbon adsorption) was the most feasible program for groundwater contaminated by a uncontrolled hazardous waste site in New England. Although biological treatment can not yet be applied to treating water supplies for direct use, it can be an efficient and cost effective part of a treatment program for water that is to be recharged into an aquifer.

Biological transformation as a treatment option for contaminated groundwater is an emerging technology. To fully utilize its potential, more research is needed to understand co-metabolism, the potential for hazardous intermediate products, interactions among bacteria and other microoganisms, biodecomposition of mixtures of organic compounds, long term transformations of resistant compounds and the effects of ozone and other factors on the biodegradability of resistant pollutants.

By innovative combinations of aerobic and anaerobic biodegradation which use properly selected microbes in an optimum environment, biological treatment is expected to have an expanded role in the treatment of contaminated groundwater.

Introduction

In situ is defined by Webster as meaning "in its original place". In the waste-and groundwater-treatment-technology literature, the term is often loosely used to refer to on-site above ground treatment. In this summary, in situ is used in its strict sense. This section describes the three classes of in situ treatment:

Physical In Situ: physical manipulation of the

water flow

Chemical <u>In Situ</u>: the injection of chemicals into

the subsurface to degrade or

immobilize contaminants

Biological In Situ: the injection of microbes and/or

nutrients to degrade contaminants in the soil/water environment

Factors Affecting Feasibility and Efficiency

In addition to all the factors that affect the feasibility and effectiveness of other treatment alternatives, in situ treatment is further affected by certain characteristics of an aquifer and the distribution (both vertical and horizontal) of the contaminant(s) within the soil and water environment.

The following conditions can pose major constraints on various $\underline{\text{in-situ}}$ treatment options: (from OTA,1984 and Josephson,1983)

<u>Aguifer Type</u>: If the contaminated aquifer is confined (or partially confined) and nonhomogeneous, it is difficult to control the injection of reagents. The contaminant and reagent may not mix thoroughly.

<u>Saturation Conditions</u>: Some degradation reactions may be limited to the unsaturated zone if aerobic conditions are required. In some parts of the Southwest, the unsaturated zone (vadose zone) can be hundreds of feet thick. This condition can be an advantage for <u>in situ</u> treatment since it would be impractical if not impossible to flush the soil and pump the contaminants out.

<u>Soil Cnemistry</u>: The soil chemistry may have an effect upon a contaminant, injected agent, or both in combination.

Flow System: Control of <u>in situ</u> reagents may be difficult after injection into recharge areas. Physical water table adjustments may be difficult in discharge areas.

<u>Depth</u>: Most <u>in situ</u> treatment programs have been conducted at shallow depths. At depths greater than 20 meters, it may be too difficult to control the movement of reagents and groundwater.

Areal Extent (Volume of Water): Once again controllability factors may limit the effective use of <u>in situ</u> methods over large areas. However, in certain cases, <u>in situ</u> may have the advantage because large volumes of water would not have to be withdrawn for treatment.

In situ treatment methods for application to groundwater restoration are in the developmental stage with few proven full scale operations. As with most remediation techniques, in situ treatment is seldom used alone, but can be a powerful tool in a well planned treatment project. For example, it is often difficult to extract strongly adsorbed contaminants from the soil environment. The slow transportation of this material into the groundwater can consequently be a long-term source of pollution. In situ degradation or immobilization of such contaminants directly in the soil environment combined with surface treatment for material already in solution can be a rapid and effective solution for many remediation problems.

Unit Process

In general, physical treatment involves adjusting the water table to enhance the effectiveness and speed of other \underline{in} \underline{situ} or above-ground treatment programs.

Applications and Limitiations

Raising the Water Table: A rise in the water table can be achieved through surface flooding, artificial recharge or through the use of infiltration ponds and wells. In some cases this induced flushing action can move contaminants out of the uns'aturated zone or isolated aquifer pockets towards a well for withdrawal and treatment. Careful consideration must be given to possible adverse effects before such action is taken (e.g. flooding or septic system failure) (OTA,1984).

Lowering the Water Table: Lowering the water table is achieved through standard pumping methods. The adjustment can increase the (unsaturated) zone of aeration and encourage aerobic digestion of amenable contaminants. Such action might also slow the downward migration of contaminants into aquifers(OTA,1984). This adjustment also has possible adverse effects that must be considered (e.g. causing near-by wells to go dry, changing the rate of recharge to an aquifer).

Another common use of artificial water table depression is in hydrocarbon retrieval (Yaniga,1982). During such recovery, a cone of depression is created that causes the "free product" (along with other dissolved contaminants) to flow towards a withdrawal pump for recovery and/or treatment (see page 26). It should be noted that after the bulk of the "free product" has been recovered, there is a body of material remaining in the unsaturated zone, in the capillary fringe area, and in association with individual soil particles. Possible treatment methods for this material (a residual contaminant source) are discussed in Biological <u>In Situ</u> Treatment Section II D.3.(page 41).

The impact of water table adjustments on contaminants found in aquifers is neither well defined nor established. Careful studies must precede a decision to use this technique.

Unit Process

The objective of chemical <u>in situ</u> treatment is to degrade or immobilize contaminants. This can be done by simple neutralization, oxidation, precipitation or polymerization.

Treatment is carried out through a series of injection wells located around or within the contaminated groundwater. A selected treatment agent is then pumped into the aquifer. A monitoring system determines the progress and effectiveness of the treatment.

Applications and Limitations

There are many theoretical applications of this technique. Ward and Lee (Canter, 1985) propose the following possible contaminant class/treatment agent relationships.

heavy metals: may be made insoluble and immobile with

alkalis or sulfides

cyanides: can be destroyed with oxidizing agents

cations: may be precipitated with various

anions or aeration

hexavalent could be made insoluble with reducing

chromium: agents

In Situ chemical treatment has had the widest application at chemical spill and hazardous waste sites. The polymerization of acrylate monomer (Williams,1982) is an example: approximately 4200 gallons of the monomer leaked from an underground pipeline. Test boring found evidence of some natural polymerization and it was decided that the process could be stimulated by chemical additives (4000 gallons of catalyst and activator for each of two treatments was used). This particular approach was adopted after careful consideration of site conditions. Although the leak took place in the unsaturated zone, the area could not be excavated because of existing buildings and underground pipelines. In spite of the many unknowns associated with this technique (see below), the in situ polymerization was attempted because it was cost effective, quickly halted further spread of the contaminant and the acrylate monomer, if left untreated, posed a present and real health hazard.

Williams cautions that this particular technique and <u>in</u> <u>situ</u> chemical treatment in general is not applicable in all situations even when it is predicted to be effective. First of all, the chemical solutions needed to bring about the desired reaction might be as harmful or even more harmful than the contaminant. Injection of these chemical solutions would then exchange one contamination problem for another. Also, a mixed

contaminant situation may require sequential injections to prevent treatment agent interactions or inhibitions. This might result in only partial treatment due to uneven dispersal of injectants.

Second, the long term effects of <u>in situ</u> chemical treatment are unknown. The possible adverse long term effects include a reduction of porosity and permeability or leaching from an unstable immobilized contaminant.

Another example of <u>in situ</u> chemical treatment cited by Canter(1985) is a commercial process called the Vyredox Method. This process, developed in Europe, removes iron and manganese from the water by <u>in situ</u> precipitation. This is achieved by pumping oxygenated water into the strata around the well. The Vyredox Method is actually a combination of <u>in situ</u> biological and chemical degradation since the injected oxygenated water not only precipitates iron directly but also encourages the growth of indigenous bacteria that preferentially oxidize iron and manganese.

A decrease in aquifer capacity due to iron deposits blocking pores in the subsurface is a common concern with the Vyredox method. Hallberg and Martinell(1976) present calculations to support an average well lifespan of 140 years based on very conservative assumptions. However, they feel that a safe estimate of well lifespan could be expanded to 750 years.

Another concern is the effect of VOCs on the performance of the Vyredox Method. The volatile organic compounds commonly found in groundwater are not readily oxidized in the absence of light so there is little competition for the injected oxygen. Although VOCs can act as toxins by degrading the membranes of microorganisms, this is not a common occurrence in the subsurface environment. Water containing VOCs up to concentrations of 100 ppb has been treated with the Vyredox Method with no adverse effect (Zienkiewicz, per. comm., 1985).

The Vyredox method has been used commercially in Europe since 1955. Since 1979, eleven plants have been installed in the United States (5 in New England). Average total treatment costs for ten US plants range from \$0.07 to \$0.20/1000 gallons (Zienkiewicz,1984).

General Note

There is a general reluctance to inject chemical reagents into an aquifer system because it is difficult to control <u>in situ</u> reactions and long term effects are unknown. For these reasons, it is generally preferred to pump and treat groundwater, and then recharge it to the aquifer.

Introduction

Subsurface biological degradation of synthetic organic contaminants has probably been a natural attentuation process ever since pollutants were added to that environment. However, this activity has only been recently appreciated and is not yet fully understood. The association of high levels of specific hydrocarbon degraders with gasoline/petroleum spills in other natural systems has been known for some time. But, because of sampling techniques, early studies of the soil below the root zone concluded that that area was devoid of life (Wilson and McNabb, 1983).

Since then, special staining and extraction techniques have been developed to identify and enumerate the microbes in the regions of shallow aquifers. The density of organisms found is similar to bacterial densities in some nutrient-rich lakes (Wilson and McNabb,1983). Interestingly, the population profile seems unique. Wilson and others could find little evidence of fungi, protozoa or higher animals in the fine grain subsurface material that was examined. This means that the scavenger roles normally taken over by protozoa in other natural systems are probably assumed by bacteria. Also, the ability to successfully inject fungi, actinomycetes, and other microbes into some subsurface environments may be limited since they don't seem to be indigenous to the vadose zone of some shallow water-table aquifers. These organisms are able to degrade or transform complex refractory organic compounds (see page 33).

In Situ application of bioreclamation has been generally limited to hydrocarbon spills or other surface spills of a single chemical. However, recent technical advances in the formulation, transport and use of supplementary nutrient solutions and an increasing understanding of the geochemical processes in the subsurface environment have renewed interest in the possibilities of this remediation technique.

This section describes the three general approaches available to this unit process and suitability criteria peculiar to <u>in situ</u> as opposed to surface biodegradation.

Unit Process

Surface and <u>in situ</u> biodegradation are in many ways two aspects of the same biological process. The reader is referred to Section II C (p.32-35) for a general discussion of aerobic and anaerobic processes, biodegradability and biodegrading organisms. Sections II D.l.(p. 38) and II D.2. (p. 39) discuss the overlaping processes of <u>in situ</u> chemical and physical treatment.

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Surface biological degradation has been used for some time to treat sewage effluent and industrial chemical waste streams. Adapted or mutated strains of bacteria are available for use with specific hazardous chemicals and methods have been developed whereby colonies of these bacteria can be stored frozen, transported and reconstituted at the contamination site. Hydrocarbon degraders have received the most media attention.

Canter(1985) lists three approaches available to <u>in situ</u> biological treatment:

- 1. Seed the subsurface environment with microbes adapted to degrade the specific pollutants(s).
- 2. Enhance the indigenous microbial population with nutrients such as oxygen sources, nitrogen, phosphorus and trace minerals.
- 3. Modify the contaminant (dispersal or emulsification) to make it more amenable to biodegradation.

These approaches are not mutually exclusive. Actual application of <u>in situ</u> biological treatment often involves all three approaches in a well planned mixture of treatment technologies.

The pumping strategy in a typical bioreclamation program controls the movement of nutrients and water through an injection, withdrawal and recharge system.

However, before these processes can be applied, biological, hydrogeological and chemical criteria must be met.

Suitability Criteria

Brubaker and O'Neil (1985) propose the following groups of compounds as amenable to subsurface biodegradation:

simple hydrocarbons aromatics (up to about three rings) compounds with one chlorine atom simple amines alcohols, esters, ketones and ethers

Wilson and McNabb (1983) also make some predictions on the prospects for biotransformation of some organic pollutants (Table 2.1). There is limited experience with these compounds in the subsurface environment. Since this is a rapidly emerging technology, these predictions may be expanded or limited as field experience is gained.

Table 2.2

Prospect of Biotransformation of Selected Organic Pollutants in Water-Table Aquifers

		ntration of ant, µg/l	
Class of Compounds	>100	<10	Anaerobic Wate
Halogenated Aliphatic Hydrocarbons Trichloroethylene Tetrachloroethylene 1,1,1-Trichloroethane Carbon Tetrachloride Chloroform Methylene Chloride 1,2-Dichloroethane Brominated methanes Chlorobenzenes Chlorobenzene 1,2-Dichlorobenzene 1,4-Dichlorobenzene 1,4-Dichlorobenzene 1,4-Dichlorobenzene Nakylbenzenes Benzene Toluene Dimethylbenzenes Styrene Phenol and Alkyl Phenols Chlorophenols Chlorophenols Chlorophenols Chlorophenols Chlorophenols Two and three rings Four or more rings	none none none none none none possible improbable probable	none none none none none improbable improbable improbable possible	possible* possible* possible* possible* possible possible possible probable none none none none none none none n

sible, prohibly incomplete.

(Wilson and McNabb 1983)

[†]Probable, at high concentration

Unlike surface biological treatment systems, the geochemical environment and presence of other organic or inorganic compounds can determine whether or not these compounds are actually degraded. For example, other organic and/or inorganic material can either inhibit the growth of bacteria or compete for their metabolic needs.

Aerobic or anaerobic conditions also determine the fate of a pollutant. For example, TCE and other halogenated aliphatic organics are not degraded in shallow aerobic aquifers but have been shown to degrade in anaerobic environments (see p. 33).

Even if the biochemical conditions are or can be made suitable (i.e. addition of nutrients or oxygen source) for <u>in situ</u> treatment, the hydrogeological characteristics of the site ultimately determine the feasibility of <u>in situ</u> biological degradation. Optimum conditions include shallow aquifers (average depth in New England is 30-100ft compared to 1000 ft or greater in SE coastal plains and SW), and permeable and homogeneous soils (uncommon in New England) which allow the rapid and controlled movement of water and nutrients (Brown et al.;1985).

Recent Advances

1. The induction into the subsurface of a consistant and adequate supply of oxygen for aerobic bacteria has been difficult to achieve in the past. Air sparging has been used but is limited by low solubility of air in water, fouling of the sparging points with biological growths and rapid depletion of available oxygen by bacteria (Yaniga and Smith,1984). Recently, the <u>in situ</u> chemical addition of oxygen into the subsurface, by means of hydrogen peroxide, has been developed to stimulate <u>in situ</u> biodegradation (Brown et al.,1984).

The levels and decomposition rate of hydrogen peroxide must be carefully controlled for a successful in situ application. Levels that are too high can be toxic to microbes and rapid decomposition rates can result in gas blocking and oxygen loss. When properly used, hydrogen peroxide can provide sufficient oxygen to increase the numbers of aerobic bacteria significantly (Brown et al., 1984). For example, Yaniga and Smith (1984) report on the <u>in situ</u> phase of the restoration of an aquifer contaminated with gasoline. Initially, air sparging was used to deliver oxygen to the subsurface. The average concentration of dissolved oxygen that could be induced into the groundwater during the first four months was only 3.4ppm. This level limited biological growth and lengthened the project timeframe. In addition, the sparging points became plugged. Laboratory and field studies were conducted using hydrogen peroxide as an oxygen donor. The dissolved oxygen stimulated microbiological growth from one to three orders of magnitude.

Methods of efficient injection of methane into the subsurface are currently being studied (WATER/Engineering and Management,1983). This would provide an environment that would stimulate anaerobic bacteria.

2. Another emerging application of <u>in situ</u> biodegradation is the treatment of volatile organic compounds. This has not been feasible in the past because the organics were present at low levels (below the critical minimum concentration) and oxygen or nutrient requirements could not be efficiently met. The understanding and evaluation of secondary utilization is an advance that has increased the practicality of <u>in situ</u> biodegradation and has made it a potentially powerful remediation tool for previously refractory compounds.

Secondary utilization is a process where-by a microbe population utilizes a secondary substrate (one below the critical minimum concentration) while its long-term energy and carbon needs are met by a primary substrate (either naturally occurring or injected).

Bouwer (1984) conducted laboratory studies using acetate as a primary substrate for microbes. Trace amounts (10-30 $\mu g/L$) of chlorinated benzenes and halogenated aliphatics were transformed (as secondary substrates) under aerobic and methanogenic conditions respectively. The author proposes that pollutants present at low concentrations might be removed from aquifers by means of secondary utilization, after injecting a primary growth-sustaining substrate and nutrients. Pilot studies need to be done to evaluate the feasibility of this approach.

<u>Applications</u>

Biological <u>in situ</u> treatment of soils and/or aquifers contaminated with petroleum products is an established commercial process. Numerous case histories in the literature document the effectiveness of this technology when combined with "free product" recovery (Yaniga, 1984; Canter, 1985; Brenoel & Brown, 1985; page 25 this report).

Frequently, the extent of pollutant remaining adsorbed to the soil in the unsaturated zone is not fully appreciated. Yaniga and Mulry (1984) have found that in general only 30-60% of the product lost during a significant spill (2000 gallons or more) is retrievable as "free product". Brenoel and Brown (1985) report a case history in which 10,000 gallons (i.e. 33%) of a 30,000 gallon gasoline spill was adsorbed to the soil particles. This adsorbed material is a continuing source of pollution as the product slowly desorbs into the water. If left to natural attentuation, the decontamination process could take

tens or hundreds of years (Brown et al., 1984). By enhancing the bioenvironment with nutrients and a source of oxygen the biodegradation process can be shortened considerably (less than five years).

A typical example of how in situ bioreclamation techniques are applied to sites contaminated with hydrocarbons was reported by Brenoel and Brown (1985). An integrated program including free product recovery, adsorbed and dissolved product treatment by enhanced bioreclamation and residual contamination removal by carbon adsorption was designed to reclaim a 30,000 gallon gasoline spill site. After 62% of the loss was recovered as free product in the first phase, enhanced bioreclamation was chosen as the second phase based on cost effectiveness, timeliness, efficiency and minimal equipment requirements. The basic elements of the second phase consisted of a circulation system to sweep the contaminated area, addition of nutrients and oxygen, and maintenance of the nutrient and oxygen levels.

Monitoring of the site after initiation of the <u>in situ</u> biodegradation program showed a 200 fold increase in hydrocarbon degraders. After 42 days the hydrocarbon levels dropped from 22,700 ppb to 581 ppb. Levels increased after this point due to an undetected leak. The carbon adsorption system reduced levels to less than 10 ppb after an additional six months of operation.

Limitations

In spite of the exciting prospects for <u>in situ</u> biodegradation, there are many limitations. The hydrogeochemical factors discussed in the introduction to <u>in situ</u> treatment (p.36) can often determine the success or failure of this approach. The potential for hazardous breakdown products can not be stressed too much. Simply monitoring for the disappearance of the target pollutant is not sufficient. Possible degradation products should be determined in laboratory studies. Monitoring for appearance of these compounds has to be part of the overall monitoring program.

Conclusions

In Situ biotechniques are potentially a powerful remediation tool for previously refractory compounds. For example, in situ degradation of TCE (one of the most ubiquitous groundwater contaminants) may be feasible within the next few years in a methanogenic environment (WATER/Eng. & Management,1985;Brubaker,1985 proceeding discussion). It remains to be seen however, if this is a complete degradation or a partial one that produces dichloroethylene or perhaps vinyl chloride (a more hazardous pollutant and potential degradation byproduct).

Public acceptance of <u>in situ</u> biological treatment of groundwater supplies is necessary. An explanation of the technology should be given with the assurance that pathological bacteria are not involved.

As current technologies are refined and understanding of pollutants in the subsurface increases, the use of <u>in situ</u> restoration programs will increase.

Introduction

Private wells are susceptible to the same pollutants that contaminate municipal wells. When contamination is discovered in a private well, a treatment decision must be made. The decision making process described in Section I (page 1) can be applied to private wells. The data collection, analysis and treatment steps are very expensive. It is beyond the scope of this summary to discuss who (state, town or individual) should assume these costs.

In general, one or more of the following options are available to the owner of a contaminated private well:

- 1. Purchase bottled water or boil water for drinking
- 2. Drill a new well
- 3. Tie into an existing municipal system
- 4. Install a point-of-use treatment system

1. Purchase bottled water

Purchasing bottled water is expensive and boiling drinking water to remove volatile organic compounds (VOCs) raises questions about the risk of inhaling vapors (Sorrell et al. 1985) In addition, these approaches do not treat water used in showers, humidifiers or vaporizers (potential sources of exposure). These measures are temporary at best. In addition, in Massachusetts, drinking water standards do not apply to bottled water.

2. Drill a new well

Depending on site conditions and the contaminant, a new well upgradient of the contaminated area may provide sufficient potable water. For example, when a well is contaminated by a nearby septic system or animal lot, relocating the well may solve the problem.

3. Tie into municipal system

Sometimes it is possible for a homeowner to arrange to receive water from an existing municipal system. In other cases, such as in Whately, Mass., new municipal systems are developed. Frequently however, no municipal system is available and it is not cost effective to develop a municipal water supply due to the size or distribution of the community.

4. Install a home treatment system

If the decision is made to install a home treatment system, the appropriate technology must be selected and a specific commercial product chosen. Due to consumer interest and a growing need to treat individual wells, there are many point-of-use products available (Consumer Reports, 1983). The most common designs include the following:

- a. faucet-mount or line by-pass activated carbon filters (PAC, solid carbon block or structured matrix)
- b. Reverse osmosis or ultra-violet combined with activated carbon
- c. air strippers

Home Treatment Systems

E.1 ADSORPTION WITH ACTIVATED CARBON FILTERS

As a consumer service, the EPA (1980) conducted a three phase study of commercially available home units containing activated carbon. This study rated unit efficiencies in terms of trihalomethane removal. In general, faucet-mounted units were found to be less effective (4-69% removal) than the line bypass units (23-99% removal). Since it is possible to run hot water through the faucet mounted units, there is the additional potential problem of desorption of contaminants from the carbon filter because of the increase in temperature.

The phase 1&2 EPA study also measured microbial and endotoxin concentrations in filter effluents of all the devices since there is a potential health hazard from bacterial growth on carbon filters during periods of non-use. Although endotoxin levels showed no increase, there was a moderate and variable increase in bacterial populations. The highest bacterial populations were found in the first water through the filter after a period of non-use (overnight or 2-5 days).

Reverse Osmosis and Ultra-Violet Activated Carbon Filters

The EPA study was expanded in its third phase to include testing reverse osmosis, ultra-violet and ozone-carbon units. However, test conditions invalidated the results. During this phase certain common organic contaminants (TCE, PCE, carbon tetrachloride and others) were added to the test groundwater filtered through the carbon units. Reductions ranged from 55% to 99% (Bell et al. 1984, EPA, 1981).

The results of this three-phase study have a very limited use. Units were tested under laboratory conditions with a selected groundwater sample and technical grade organic compounds. The effectiveness and performance of these commercial in-home-units should still be considered unknown for any specific well site.

Recently, a packed tower (see p. 9) aeration system for home wells was put on the market (VOX-OUT, PSC Water Products Inc.). The manufacturer provided no scientific data to back claims of 90% removal of most commonly detected VOCs in groundwater (see page 9 for discussion of difficulty in interpreting results given in terms of percent removal alone). Since the system is designed to run continuously and "return treated water to the well by gravity for storage" (product literature), it is unclear how many times the water must pass through the 5 1/2 ft tower before being completely decontaminated. Also, the "off-gas" would need to be properly vented.

A bubble aeration system (see p. 8) has been recently developed by Lowry and Lowry (1985). The system was designed to treat household water supplies contaminated with gasoline. In one reported field installation, water with 362ppm gasoline was treated to less than 4ppb (detection level).

Another home air stripper is in the experimental stage and test data should be available soon (G Moore, U. of Mass. Amherst, per. comm. 1985).

Applications and Limitations of Home Units

Carbon adsorption and air stripping are proven unit processes for treating some contaminated groundwater on a large scale. The technology is being adapted for efficient and reliable performance in point-of-use units as either permanent or interim treatment. The installation of home treatment units may prove to be more efficient and cost effective than developing a municipal water supply in some cases. Much more design, operational and economic data is necessary before this option can be fully evaluated.

Manufacturers must provide sufficient data before any home treatment system can be properly evaluated. If product test results are available they must be evaluated in terms of extent of testing and detection limits of the tests. However, without the necessary scientific and engineering expertise, it is often difficult or impossible for an individual well owner to determine how effective any given device is for a specific site.

The EPA's study and recent National Sanitation Foundation standards (NSF, 1982) offer some guidance. More study is required to resolve questions regarding potential health risks from bacteria released from carbon filters and the long term

performance of these systems before they can be considered an available alternative to central treatment. Since no one is offering "off-the-shelf" treatment units for municipal water supplies, one should be cautious of such units for point-of-use treatment of private wells contaminated with hazardous organic compounds.

The performance of point-of-use treatment units is affected by the uncertainties associated with individual responsibility for maintenance and monitoring as well as the hydrogeologic and chemical complexities of each situation. After choosing the unit that best meets removal requirements, it is essential that proper maintenance and monitoring be performed to assure continuing performance. If the unit is used improperly or not maintained, the users may be exposed to increased levels of contaminants. Some form of registration and maintenance service might be necessary to assist the owner with operation and maintenance.

MATRIX 1: GROUNDWATELY FIREAUT ALTERNATIVES VERSUS VARIOUS PARVAETERS

Special Notes/Commuts					
Availability of Technology	Comercial		Comercial	Pilot studies	Commercial
Limitations	- Does not remove non- volatile organics - May require treatment of off gas	- does not remove non-volatile organics - may require treatment of off gas	- red virgin carbon for pot- able water - low m.w. compounds (VOCs) prorly adsorbed - requires complex monitoring program - subject to competitive ad- sorption - spert carbon requires dis- posal	- mt. well tested - subject to fouling and membrane deterioration - high cost	- des not remove dissolved contaminants - can change character of water for subsequent treatment
Applications	- Removes volatile organics (VOCs) with high efficiency - Relatively simple to operate	- Removes volatile and semi- volatile organics	- Removes a wide range of adsorbable organics - no air emissions - removes high boiling point compounds	- may be able to remove volatile nompolar compounds - may achieve low effluent levels - on site regeneration may be possible	- removes suspended material - may remove IHM precursors
Freaturent Alternatives	A. Physical Treatment A-1. Stripping a. Anhient air	b. Steam (high tamperature)	A-2 Msorption a. Activated carbon	b. Synthetic resin	A-3 Filtration

MATRIX 1: GROUNDWATER TREATMENT ALTERNATIVES VERSUS VARIOUS PARAMETERS (Continued)

Special Notes/Communts						
Availability of Technology	Commercial-inorganics R & D-organics	Connercial	Comercial	Commercial	Commercial	Commercial
Limitations	- does not retain low mol. wt. compounds - generates concentrated aqueous waste that needs disposal mixtures of solutes decrease effectiveness - mixtures of solutes decrease effectiveness - mixtures of solutes decrease effectiveness	- can not remove hydrocarbons adsorbed to soil or dis- solved in groundwater		- docs not remove hazardous	- chūmical additives must be carefully selected	
Applications	- removes a wide range of inorganic compounds - might be useful in preparing water samples for analysis	- removes floating hydrocarbons (free product)	- removes colloidal solids and heavy metals - may remove THM precursors	- removes inorganic ions	- convert compounds to less toxic forms or to carbon dioxide	 precipitate some metals with proper pH decrease corrosive character of water control rate & direction of reactions
Treatment Alternatives	A-4 Reverse Osmosis	A-5 Skimning	8. Chanical Treatment 8-1 Cosquistion/ Claiffication	8-2 Ich exchange	8-3 Chomical Frans- formation a. Chomical oxidation	b. pdl adjustment

GROUNDWATER TREATMENT ALTERNATIVES VERSUS VARIOUS PARAMETERS (Continued) MMRIX 1:

Special Notes/Communits	- low temperatures slow program	- low temperatures slow process	- most effective in unconfinct bymogeneous aquifers - difficult to do in discharge area	Temperatures: - soil temperatures below freezing may inhibit chemical reactions - air temperatures below freezing require special hardling	Aquifers: - reagents may be difficult to control after injection in recharge areas - limited experience at or	below 20 meters
Availability of fechnology	3	Emerging connercial	Emerging commercial	Commercial		
Limitations	- can not currently remove	- anaerobic systems relatively slow - may produce hazardous inter- mediate product - pollutants need to be at minimum levels - aerobic systems require aeration and produce sludge which requires disposal	- effect on contaminants not fully understood	- chamicals injected may be hazardous - long-term leaching unknown	- injectant interactions un- known - potential decrease in poro- sity and permeability - requires extensive moni- toring - difficult to treat if con-	taninants are at low con- centrations or widely
Applications	- treat biodegradable organics	- degrade organics not amenable to aerobic degradation	- soil flushing by raising water table - retain pollutants in unsaturated zone by lowering water table	- neutralizes but does not remove acids or bases	- can immobilize certain or- ganic compounds with more than one double bond	- Inorganics
Treatment Alternatives	C. Biological Treatment C-1 Acrobic Degrada-	C-2 Anaerdbic Degrada-	D. In-Silu Treatment D-1 Physical Manipula- tion Water Table Adjustment	0-2 Chomical Trans- formation a. Moutralization	b. Polymerization	c. Precipitation

GROUNDWATER TREATHEM ALTERNATIVES VERSUS VARIOUS PARAMETERS (Continued) MTRIX 1:

Special Notes/Communic	Temperatures: - low groundwater temperatures may affect rates - soil temperatures helev freezing may inhibit or kill microbes Aquifers: - may be restricted to uncaturated zone if dependent or aerobic conditions - reagents may be difficult to control after injection in pechange areas - limited experience at or below 20 meters - permeable and homogeneous soils needed for obtiment control		
Availability of Technology	Comercial	Comercial	Commercial
Limitations	- possible formation of hazardrus degradation product requires extensive monitoring reduction to ppm levels generally restricted to organic compounds rot effective when contaninant levels are extremely high or low	- system used and maintained by untrained persons - potential for bacterial growth on filters - culire water supply may not be treated - risk of exposure through showers etc contaminated carbon filters must be properly disposed competitive adsorption and desorption of some	- systems used & maintained by untrained persons - system size limitations - cannot remove semi- or non-volatile organics - generates off-gas
Applications	- does not require removal of large volumes of water-useful for abandoned wells - adapted or muta ted introduced strains can degrade some naturally resistant compounds	- removes a wide range of volatile compounds	- removes highly volatile organic compounds - not affected by mixtures of pollutants
Treatment Alternatives	Degradation	E. Point-of-Use-Treatment E-1 Carton Adsorption	E-2 Air Stripping

CLASSES OF COMPOUNDS VERSUS APPLICABLE TREATMENT FECHNOLOGIES¹ MATRIX 2:

CLASSES OF COMPOUNDS VERSUS APPLICABLE TREATMENT TECHNOLOGIES¹ (Continued) MATRIX 2:

		Treatment	Treatment Process ²	
Class of Compound	Carbon Adsorption3	Stripping	Biological	In-Situd
3. Alcohols				Yes
a. Methanol	No	Yes, high temp., low efficiency	Yes	Biological (theoretical)
b. Isopropanol	No	Yes, high temp., low efficiency	Yes	Biological (theoretical)
4. Ether's	Yes	Yes	Yes	
5. Ketones, Aldehydes				
a. Methylketone (MEK)	Yes	Yes (steam)	Yes	Biological
Herbicides, Pesticides	Yes	Yes	Yes	Biological
1. EDB (Ethylene Dibromide)	Yes	Yes (difficult)		
2. Temik (Aldicarb)	Yes			

Sources: Absalon & Hockenbury, 1983; OTA, 1984; Personal Communications Specific organics within a class may not follow these general treatment guidelines Specific organics within a class may require large, impractical amounts of carbon Many specific organics within a class have not yet been tested.

^{4.3.5.1}

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Introduction

The cost of treating contaminated groundwater is a major consideration in any aquifer restoration decision. Groundwater treatment costs are necessarily site specific and difficult to generalize. One survey found that contaminated water treatment at Superfund sites ranged from \$0.017/gallon to \$4.60/gallon (Young, 1983). Many site and design factors combine to make each treatment program unique.

Treatment costs of specific systems are sometimes cited in product literature, journal articles or symposium proceedings. However this scattered information is not uniformily derived and is therefore difficult to compare.

Various attempts have been made to summarize costs of selected technologies in order to provide concise and understandable cost data (DeWolf et al.,1984 and Clark & Eilers,1982). However, these reports can only provide general guidelines in what is a very site specific process.

In spite of these constraints, useful cost data that are available, and the factors that affect such costs, are presented here in order to provide some basis on which to evaluate proposed treatment alternatives. However, before any final selection is made, a detailed cost analysis should be done on each treatment option for the specific site in question. Cost ranges for the following treatment methods are discussed in this section: l.stripping(packed tower), 2.carbon adsorption (see p.20 for resin adsorption costs), 3.carbon vs stripping. 4.carbon vs biodegradation, 5.conventional filtration, 6.reverse esmosis, 7.skimming, 8.in situ, and 9.point-of-use.

Full scale field experience in treating contaminated groundwater supplies is still very limited at this time. However, as more treatment systems become commercially available, competition should provide cost effective (but still very expensive) treatment that meets health and environmental requirements.

PREVENTION OF GROUNDWATER CONTAMINATION IS STILL THE MOST EFFECTIVE AND LEAST EXPENSIVE TREATMENT.

Pantors That Affect Treatment Costs

The following lactors affect the cost of any aquifer treatment program:

- 1. Chosen technology(ies)
 - a. capital cost
 - b. operation and maintenance cost (0&M)
- 2. Contaminant(s) present
 - a. nature of contaminant(s)
 - b. concentration(s)
 - c. possible mixture interactions and/or competitions
 - d. profile over time(expected increase or decrease over time at point of withdrawal
- 3. Removal criteria
 - a. present requirements
 - b. possible revised future requirements
- 4. Other water quality characteristics
 - a. presence of iron, manganese or other metals
 - b. pH
 - c. temperature
- 5. Existing treatment facilities
- 6. System capacity
- 7. Time in operation

Other factors that affect costs of specific treatment techniques are discussed in the pertinent section.

1. Chosen Technology

Capital and O&M are the two cost components of any particular treatment technology. Some options require high capital investments but have relatively low O&M costs. All things being equal, this option would be more cost effective for a lengthy treatment program than an option with a low capital cost but a high maintenance cost.

2. Contaminants Present

The nature of a contaminant (volatile or non-volatile, biodegradable or refractory) determines in general which treatment options are applicable. In addition, some treatment methods are more sensitive than others to the pollutant concentrations and lose the cost competitive edge when concentrations get high. Mixtures of contaminants at various concentrations (a common characteristic of contaminated groundwater) often compete for removal or prevent a treatment option from achieving total removal of all contaminants.

The concentration profile over time can also determine the cost effectiveness of any particular treatment method. A two-phase treatment system might be the most cost effective if concentrations are expected to drop over time. On the other hand, the best choice for present conditions might prove to be too expensive if concentrations increase with time. A thorough analysis of the contamination plume and hydrogeology can prevent financial surprises in this regard.

3. Removal Criteria:

A chosen method might be cost effective for present removal objectives but too expensive or not adaptable for possible future more stringent removal requirements. Techniques are constantly being improved to detect more types of organic chemicals and at lower limits (parts per quadrillon for some non-volatiles). Research is finding more and more of the groundwater contaminants to be possible carcinogens. The public may soon be unwilling to accept any detectable amounts of pollutants in their water supplies and treatment costs will be affected accordingly.

4. Other Water Quality Characteristics:

Frequently, attention is so focused on the organic contaminants in a water supply that other aspects of the water quality are ignored or assumed to be self correcting. Pretreatment can add considerable cost to any project proposal but may be essential to the long term performance and efficiency of the primary treatment system. For example, if high levels of iron and manganese are present in the groundwater, iron and manganese oxide can clog carbon filters or aeration packing if not removed or kept in solution. A treatment proposal that does not address other water quality components in addition to the target contaminants is incomplete.

5. Existing Treatment Facilities:

If a water supply has a conventional treatment facility, it might be possible to reduce costs by modifying the existing plant to remove the pollutant in question or modify the water (lime addition etc.) in a pretreatment step.

6. System Capacity:

Many of the treatment options become more cost effective with increasing size. Groundwater supply wells are generally small capacity wells that are widely dispersed. However, the possibility for combining treatments for nearby wells should always be considered, as well as regionalization of supply and treatment to achieve economy of scale.

7. Time In Operation:

Many treatment programs last several years or longer. The cost of operation over the entire length of the treatment program should be considered. For example, energy costs for aeration towers or cost of carbon replacement contracts might increase dramatically midway through the treatment period.

Although state and Federal funding is very limited at this time, short sighted or "small budget" remediation projects may prove to be very expensive if in the future they have to be expanded or redone.

1. Tower Aeration Costs

Basin aeration is less efficient and more expensive than tower aeration (DeWolf et al.,1984). Nost of the available cost information is for the tower aeration design which is the only design discussed in this section. The major variables affecting costs for tower aeration treatment are: column height, system temperature, air/water ratios, flow rate and "off gas" treatment.

One manufacturer reports that total treatment costs (amortized capital and 0&M) for trichloroethylene(TCE) range from \$0.04-\$0.06/1000 gallons treated (Lenzo, Hydro Group, per, comm.,1985). TCE is one of the most common VOCs found in groundwater and represents average costs for removal of chlorinated solvents. This same manufacturer goes on to say that the system cost for his most expensive operating air stripping unit is approximately \$0.17/1000 gallons.

Total aeration costs for trihalomethane removal by aeration are given in Figure 3-1. The major design parameters for 90% removal are:

air/water ratio 100:1 operating temperature 70-80°F tower height 22 feet influent chloroform 10-800mg/L

The cost is approximately 0.17/1000 gallons for a 1.0 million gallon per day (mgd) system.

Acration for prinking water treatment - Unit annualized cost (March, 1950 pollars).

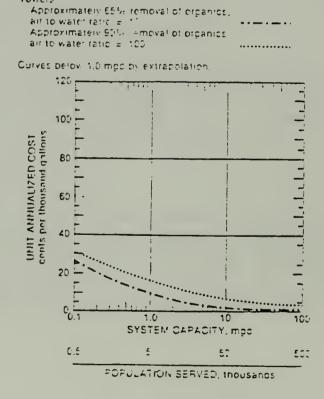
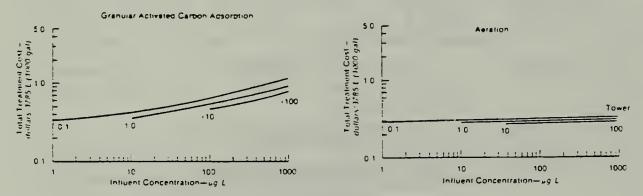


Figure 3-1. Aeration Costs-Trihalomethane Removal (DeWolf et al. 1984)

No cost information was available for steam stripping or "off gas" treatment at this time. However, informal conversations with three consultants revealed that steam stripping (even if combined with "off gas" treatment) would be competitive with carbon adsorption for the same site.

2. Carbon Adsorption Costs

The major factors that affect costs withing a GAC design are "contact time" (see p.17), carbon loading, and carbon replacement frequency. Compared to aeration, GAC is very sensitive to the influent concentration of a contaminant as well as its adsorbability (see fiq. 3-2).



Cost of trichloroethylene removal

October 1980 dollars: effluent concentrations of 0.1-100 µg/L: design flow of 1.8 ML/d (0.5 mgd) operating at 60 percent capacity: numbers in parentheses are effluent concentrations in µg/L

Figure 3-2. Carbon Adsorption and Aeration Costs Versus Influent Concentrations (After Love and Eilers, 1982) Reprinted from Journal AWWA, Vol. 74,No. 8 (August 1982), by permission. Copyright @ 1982, The American Water Works Association.

O'Brien and Fisher(1983) state that operating costs for GAC adsorption range from \$0.22-\$2.52/1000 gallons depending on influent concentration (fiq. 3-3).

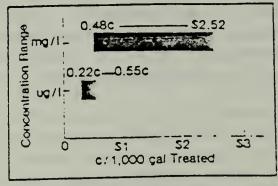


Figure 3-3. Granular carbon operating costs for groundwater treatment.

Reprinted with permission from Water Engineering & Management, Way 1983.

Love and Eilers (1982) give some theoretical treatment costs for GAC adsorption of TCL. These costs range from \$0.55-\$2.00/1000 gallons for 99% removal (fig. 3-4).

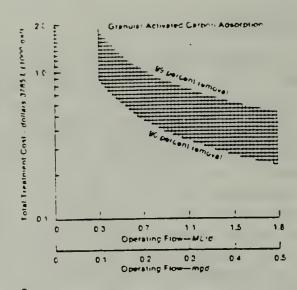


Figure 3-4. Cost of trichloroethylene removal (90-99 percent)

October 1980 dollars; influent concentration of 1-1000 µg/L: design flow of 1.8 ML/d (0.5 mgd)

(After Love and Eilers, 1982) Reprinted from Journal AWWA, Vol 74, No. 8 (August 1982), by permission. Copyright @1982, The American Water Works Association.

3.GAC Versus Air Stripping Costs

When a contaminant is amenable to removal by only one technology, cost considerations are simply a matter of choosing the most efficient and cost effective system design within that However, removal capabilities of some treatment method. technologies overlap for many contaminants. For example, there has been much discussion of the merits of GAC versus air the most common organic stripping for the removal of contaminants found in groundwater. In these cases, thorough pilot studies (see p.3) and accurate cost estimates, in addition to the prior experience of any particular investigator, play important roles in the selection process.

It is generally difficult to compare full scale operations because site conditions are not the same. However, the opportunity to compare two different full-scale operations that removed the same contaminants at the same site has been provided by Rockaway Township, New Jersey (McKinnon & Dyksen, 198+; ACCM, 1981). A GAC adsorption system was initially

installed in October, 1980 to remove TCE and two ethers. However, after four months, ethers appeared in the effluent and required more frequent carbon replacement due to rapid breakthrough (replacement every 45 days rather than the estimated every 130 days). A packed tower air stripper was installed in December 1981 that removed all of the ethers and almost all of the TCE. A cost comparison of these two systems is given in Table 3-1.

Air Stri	pping	Granular Activated Carbon		
Item Total Cos	t Annual Cost	Item Total Cost	Annual Cost	
Capital* \$375,000 (Equipment & Insta		Capital* \$200,000 \$23,492 (Equipment & Installation)		
Operating Cost \$80,000 (Power @ \$.09/KWH)		Operating Cost (Carbon recharges @ 6 week intervals @ \$32,000 ea.)	\$277,000**	
Total Annual Cost	= \$124.047	Total Annual Cost =	\$300,492	

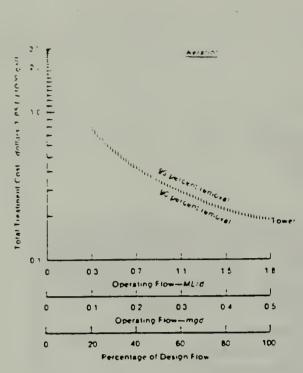
Annual labor costs for operation are minimal since both systems are automatic.

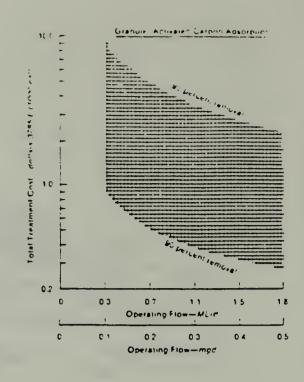
Table 3-1. Comparison of Stripping and Carbon Adsorption Costs For Removal of TCE and ethers at Rockaway Township, N.J. (From Product Literature, Hydro Group) Reprinted by permission.

Frequently, two treatment methods are cost competitive at a lower percent removal of certain compounds but one method becomes prohibitively expensive at a higher percent removal. For example, the cost of 90% versus 99% 1,1,1 trichloroethane removal by aeration or GAC adsorption is shown in fiq. 3-5. At 90% removal the cost is about the same for both methods (\$0.35-\$0.40/1000 gallons /0.3mgd). However, to remove 99% of the trichloroethane by GAC adsorption costs approximately 3 1/2 times as much as 99% removal by air stripping(\$0.35 versus \$1.25/1000 gallons/0.3mgd).

^{*}Capital costs amortized over 20 yrs. at 10% interest rate.

^{**}Some labor required for carbon recharges, not included.





Cost of 1,1,1-trichloroethane removal (90-99 percent)

October 1980 dollars; influent concentration of 1-1000 µg/L; design flow of 1.8 ML/d (0.5 mgd)

Figure 3-5. Comparison of Aeration and Carbon Adsorption Costs: 90% versus 99% Removal of 1,1,1-trichloroethane (After Love and Eilers, 1982) Reprinted from Journal AWWA, Vol 74, No. 8 (August 1982), by permission. Copyright @ 1982, The American Water Works Association.

4. Carbon Adsorption Costs versus Biological Degradation

Another informative cost analysis compared above ground biological degradation to GAC adsorption treatment for groundwater contaminated by a Gulf Coast hazardous waste landfill (Nyer and Sauer, 1984). This report exemplifies a thorough site analysis in which conditions over the entire life cycle of the treatment program were considered.

The treatment program was limited to contaminated groundwater (total organic carbon, TOC, 1300mg/L, phenol 400 mg/L) in a shallow saturated zone. The objective was to treat to recharge quality(TOC:18mg/L, phenol:0.2mg/L). The cost analysis considered treatment costs over a range of concentration since the influent organic concentration was expected to decrease with time.

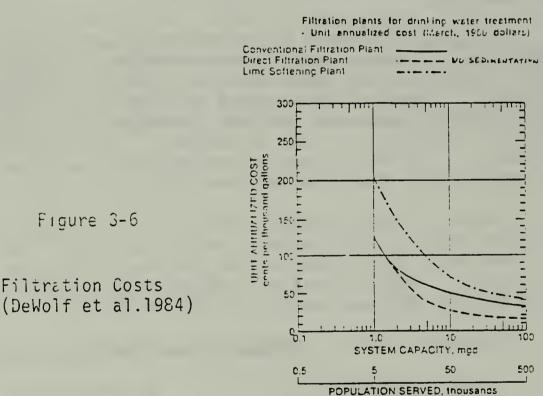
A major factor affecting the use of biological treatment was operating costs attributed to personnel. Carbon adsorption systems require negligible attention compared to biological degradation systems. Even if it required attention around the clock, however, the study concluded that biological treatment would cost approximately one-fourth as much as carbon

adsorption. As the influent concentration decreased with time it was determined that the activated sludge system would not be able to adapt and therefore GAC would become the most cost effective as well as most efficient choice.

Therefore, in the above case, technical and cost considerations were combined to develop a multi-stage treatment design that included two types of biological treatment (activated sludge followed by fixed film) and GAC to achieve the required effluent concentration while the influent concentration decreased.

5. Filtration Costs

There are many combinations of various process steps possible in filtration plants. However, the major factor affecting cost is the filter design. As can be seen from figure 3-6, filtration can range from \$1.25 to \$2.05 /1000 gallons for a small system. Unlike surface water supplies, most groundwater supplies do not require treatment other than chlorination. If pretreatment is a necessary step in an aquifer restoration program, it can possibly double the cost of treatment.



6. Reverse Osmosis (RO) Costs

The major factors that determine the cost of this treatment method are 0&M, membranes, chemicals and treatment objectives. Eisenberg and Middlebrook (1984) surveyed on-line RO plants and found that total operating costs ranged from \$1.50 to \$4.85/ 1000 gallons. Capital costs ranged from \$20,000 to \$8,500,000 depending on plant capacity.

An average cost for skimming systems is not available due to the site specific nature of system designs and operations. However, some factors that affect the cost of free product removal are mentioned here in order to help the reader better evaluate project proposals:

- 1. The amount of hydrocarbon on the water table
- 2. The speed at which the hydrocarbon is coming into the well (high yield or low yield aquifer)
- 3. The time of the spill (if the spill is recent, product hasn't migrated too far and therefore might not require many recovery wells.

These factors affect the choice of system, system capacity and time in operation--all of which affect the cost (Reed, 1985, per.comm.).

One case history discussed in the literature (Littlefield et al. 1984) has a to-date cost of \$5/gallon of recovered oil. The cost is expected to increase as oil production declines due to migration of the product.

8. In Situ Costs

In Situ treatment for aquifer restoration is an emerging technology. There is very little information available on full scale operations and even less on the cost ranges for such treatment. Some of the factors that would affect the cost of this treatment approach are the hydrogeology, chemistry and microbial activity of the subsurface. Well installation is expensive. If many injection and monitoring wells are needed, the cost could be very high (Nielsen, 1982).

Enhanced bioreclamation (see p.42) is one type of <u>in situ</u> treatment that is offered on a commercial basis. The elements and associated cost ranges of one patented process are given in Table 3-2. Capital investment ranges from \$65,000 to \$265,000 with a monthly O&M cost range of \$5,000 to \$20,000.

Table 3-2 Bio XL Enhanced Bioreclamation Program

Site Assessment	\$5,000-\$15,000			
Process Design	\$10,000-\$100,000			
Program Implementation	\$50,000-\$150,000			
Total Capital Investment	\$65,000-\$265,000			
O&M (monthly)	\$5,000-\$20,000			

(From product literature 1985 FMC Corp. Princeton, N.J.)

S. Point-Of-Use (Home theatment) Costs

Point-of-use carbon adsorption systems are enpensive. After capital investments from \$25 to \$900, maintenance costs range from \$6.00 to \$40.00/1000 gallons treated (Consumer Reports, 1983; Thomas, S.F., 1985, per. comm.).

Clark and Eilers(1982) have frequently been quoted to support the cost effectiveness of home treatment carbon adsorption devices in certain cases. However, the cost assumptions were based on unrealistic water usages (8 gal/family day), and design life(10 years).

Capital costs for home air stripping systems are expected to be in the \$1000 to \$2500 range. O&M costs are \$10-18 per month (Lowry& Lowry,1985, proceeding discussion; PSC Water Products, product lit.).

The need for installation and maintenance of a pretreatment system (e.g. iron and manganese removal) would add to the overall cost of any home treatment unit.

In light of the relatively low proposed costs for home aeration systems, installation of individual aeration treatment units (that meet and maintain drinking water standards) might be an alternative to developing a municipal water system in certain circumstances. However, much more performance and economic information is necessary before this option can be fully evaluated.

TABLE OF ESTIMATED COST RANGES FOR GROUNDWATER TECHNOLOGIES

Highest Available Quoted Costs for Technology	\$0.17/1000 gallons	\$2.52/1000 gallons	\$4.85/1000 gallons			\$40/1000 gallons (0 & H)
Cost Ranges	\$0.04-\$0.06/1000 gall. (total costs) (1985 dollars)	\$0.55-\$2.00/1000 gallons (1983 dollars)	\$1.50-\$4.85/1000 gallons (0 & H) (1981 dollars)	\$1.25-\$2.05/1000 gallons (0 & H) (1981 dollars)	\$5,000-20,000/month (0 & H) (1985 dol.) \$65,000-\$265,000 (Capital)	\$6.00-\$40.00/1000 gall. (0 & M) (1983 dollars)
Example Pollutant	Trichloroethylene	Trichloroethylene	Inorganics	Conventional Treatment	Biodegradable Organics	Range of Organics
Technology	Packed Tower Air Stripping	Carbon Adsorption	Reverse Osmosis	Filtration	In Situ (Biological)	Point-of-Use Carbon

 $^{
m l}_{
m NOTE}$: The costs of some of the above listed technologies can not be directly compared.

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APPENDIX A

ORGANICS KNOWN TO OCCUR IN GROUNDWATER

Contaminant	Examples of uses ^d		
Aromatic hydrocarbons			
Acetanilide	Intermediate manufacturing, pharmaceuticals, dyestuffs		
All yl benzene sulfonates	Detergents		
Aniline	Dyestuffs, intermediate, photographic chemicals, pharmaceuticals, herbicides, tungicides, petroleum relining, explosives		
Anthracene	Dyestuffs, intermediate, semiconductor research		
Benzene	Detergents, intermediate, solvents, antiknock gasoline		
Benziaine	Dyestuffs, reagent, stillening agent in rubber compounding		
Benzyl arcohol	Solvent, perfumes and flavois, photographic developer inks, dyestuffs, intermediate		
Butoxymethylbenzene	NA '		
Chrisene	Organic synthesis		
Crecsote mixture	Wood preservatives, disinfectants		
Dibenz[a.h.]anthracene	NA NA		
Di-butyt-p-benzoguinone	NA		
Dihydrotrimethylquinoline	Rubber antioxidant		
4.4-Dinitrosodiphenylamine	NA		
Ethylbenzene	Intermediate, solvent		
Fluoranthene	NA		
Fluorene	Resinous products, dyestuffs, insecticides		
Fluorescein	Dyestuffs		
Isopropyl benzene	Solvent, chemical manufacturing		
4.4'-Methylene-bis-2-chloroaniline (MOCA)	Curing agent for polyurethanes and epoxy resins		
Methylthiobenzothiazole	_		
Naphthalene	Solvent, Jubricant, explosives, preservatives, intermediate, fungicide, moth repellant		
o Nitroaniline	Divestuffs, intermediate, interior paint pigments, chemical manufacturing		
Nitropenzene	Solvent, polishes, chemical manufacturing		
4-Nitrophenol	Chemical manufacturing		
n-Nitrosodiphenylamine	Pesticides, retarder of vulcanization of rubber		
Phenanthrene	Dyestuffs, explosives, synthesis of drugs, biochemical research		
n.Propythenzene			

1.2.4-Trimethylbenzene

Styrene (vinyl benzene)

Xylenes (m.o.p)

n-Propylbenzene

Pyrene

Toluene

Oxygenated hydrocarbons Acetic acid

Food additives, plastics, dyestuffs, pharamaceuticals photographic chemicals, insecticides

Plastics, resins, protective coatings, intermediate

Adhesive solvent in plastics, solvent, aviation and high octane blending stock, dilutent and thinner, chemicals,

Manufacture of dyestuffs, pharmaceuticals, chemical

Aviation gasoline, protective coatings, solvent, synthesis of

Dyestuffs, solvent

manulacturing

organic chemicals

Biochemical research

explosives, detergents

APPENDIX A

ORGANICS KNOWN TO OCCUR IN GROUNDWATER - continued

Contaminant

Oxygenated hydrocarbons (cont'd)

Acetone

Benzophenone
Butyl acetate
n-Butyl-benzylphthalate
Di-n-butyl phthalate

Diethyl ether

Diethyl phthalate Diisopropyl ether 2.4-Dimethyl-3-hexanol 2.4-Dimethyl phenoi

Di-n-octyl phthalate 1.4-Dioxane

Ethyl acrylate Formic acid

Methanol (methyl alcohol) Methylcyclonexanone Methyl ethyl ketone

Methylphenyl acetamide Pnenols (e.g., pTen-butyiphenol)

Prinalic acid 2-Propanoi

2-PropvI-1-heptanol Tetranyorofuran Varsol

Hydrocarbons with specific elements (e.g., with N,P,S,CI,Br,f,F)
Acetyf chloride
Afachlor (Lasso)
Aldicarb (sulfoxide and sulfone;

Temik)
Afdrin
Atrazine
Benzoyl chloride
Bromacil
Bromobenzene

Examples of uses^d

Dyestuffs, solvent, chemical manufacturing, cleaning and drying of precision equipment

Organic synthesis, odor fixative, flavoring, pharmaceuticals Solvent

Plastics, intermediate

Plasticizer, solvent, adhesives, insecticides, safety glass, inks, paper coatings

Chemical manufacturing, solvent, analytical chemistry, anesthetic, pertumes

Plastics, explosives, solvent, insecticides, perfumes Solvent, rupper cements, paint and varnish removers Intermediate, solvent, fubricant

Pharmaceuticals, plastics, disinfectants, solvent, dyesfuffs, insecticides, fungicides, additives to lubricants and gasolines

Plasticizer for polyvinyl chloride and other vinyls Solvent, lacquers, paints, varnishes, cleaning and detergent preparations, fumigants, paint and varnish removers, wetting agent, cosmetics

Polymers, acrylic paints, intermediate

Dyeing and finishing, chemicals, manufacture of fumigants, insecticides, solvents, plastics, refrigerants

Chemical manufacturing, solvents, automotive antifreeze, fuels Solvent, Jacquers

Solvent, paint removers, cements and adhesives, cleaning fluids, printing, acrylic coatings

Na

Resins, solvent pharmaceuticals, reagent, dyestuffs and indicators, germicidal paints

Dyestuffs medicine, periumes, reagent

Chemical manufacturing, solvent, delicing agent, pharmaceuticals, periumes, lacquers, dehydrating agent, preservatives

Solvent Solvent

Paint and varnish thinner

Dyestuffs, pharmaceuticals, organic preparations Herbicides Insecticide, nematocide

Insecticides

Herbicides, plant growth regulator, weed control agent

Medicine, intermediate

Herbicides

Solvent, motor oifs, organic synthesis

ORGANIOS KNOWN TO OCCUR IN GROUNDWATER - continues

Contaminant

Examples of uses?

hvolocarbone with specific elements (e.g., with N.P.S.Cl.Br.J.F) (contid) Bromochloromethane Bromodichloromethane Bromolorm Carboluran Carbon tetrachloride

Chlordane
Chlorobenzene
Chloroform
Chlorohexane
Chloromethane (methyl chloride)

Chloromethyl sullide 2-Chloronaphthaiene

Chlorbyrifos
Chlorthal-methyl (DCPA, or Dacthal)
o-Chlorotoiuene
p-Chlorotoiuene
Dibromochloromethane
Dibromochloropropane (DBCP)
Dibromodichloroethylene
Dibromoethane (ethylene
dibromide, EDB)
Dibromomethane
Dichlolenthion (DCFT)
o-Dichlorobenzene

p-Dichlorobenzene

Dichlorobenzidine
Dichlorocyclooctadiene
Dichlorodiphenyldichioroethane
(DDD, TDE)
Dichlorodiphenyldichloroethylene
(DDE)
Dichlorodiphenyltrichioroethane
(DDT)
1.1-Dichloroethane

Fire extinguishers, organic synthesis

Solvent, lire extinguisher Iluid, mineral and salt separations

Solvent, intermediate Insecticide, nematocide

Degreasers, refrigerants and propellants, fumigants, chemical

manufacturing

Insecticides, oil emulsions

Solvent, pesticides, chemical manufacturing

Plastics, fumigants, insecticides, refrigerants and propellants

NA

Refrigerants, medicine, propellants, herbicide, organic

synthesis

NA

Oil: plasticizer, solvent for dyestuffs, varnish gums and

resins, waxes

wax: moisture, Ilame, acid, and insect-proofing of fibrous materials; moisture, and flame-proofing of electrical cable;

solvent (see oil)

Herbicide

Solvent, intermediate Solvent, intermediate Organic synthesis Fumigant, nematocide

NA

Fumicant, nemalocide, solvent, waterproofing preparations,

organic synthesis. Solvent

Pesticides

Solvent, fumigants, dyestulfs, insecticides, degreasers,

polishes, industrial odor control

Insecticides, moth repellant, germicide, space odorant,

intermediate, lumigants

Intermediate, curing agent for resins

Pesticides Insecticides

Degradation product of DOT, found as an impurity in DOT

residues Pesticides

Solvent, fumigants, medicine

ORGANICS KNOWN TO OCCUR IN GROUNDWATER - continued

Contaminant

Examples of useso

Hydrocarbons with specific elements (e.g., with N,P,S,Cl,Br,I,F) (cont'd) 1,2-Dichloroethane

1,1-Dichloroethylene (vinylidiene chloride)
1,2-Dichloroethylene (cis and trans)

Dichloroethyl ether

Dichlorolodomethane
Dichlorologoropylether (= bis-2chlorologoropylether)
Dichloromethane (methylene
chloride)
Dichloropentadiene
2.4-Dichlorophenol
2.4-Dichlorophenoxyacetic acid
(2,4-D)
1.2-Dichloropropane

Dieldrin
Diiodomethane
Diisopropylmethyl phosphonate
(DIMP)
Dimethyl disulfide
Dimethylformamide
2.4-Dinotrophenol (Dinoseb,
DN&P)
Dioxins (e.g., TCDD)
Dooecyl mercaptan (lauryl mercaptan)
Encosultan
Encrin

Eis-2-etnylhexylphthalate Di-2-etnylhexylphthalate Fluorobenzene Fluoroform Heptachlor Heptachlorepoxide

Einyl chloride

Hexachlorobicycloheptadiene Hexachlorobutadiene Solvent, degreasers, soaps and scouring compounds, organic synthesis, additive in antiknock gasoline, paint and finish removers

Saran (used in screens, upholstery, fabrics, carpets, etc.), adhesives, synthetic fibers

Solvent, perfumes, lacquers, thermoplastics, dye extraction, organic synthesis, medicine

Solvent, organic synthesis, paints, varnishes, lacquers, finish removers, drycleaning, fumigants

NA

Solvent, paint and varnish removers, cleaning solutions

Solvent, plastics, paint removers, propellants, blowing agent in foams

NA

Organic synthesis

Heroicides

Solvent, intermediate, scouring compounds, fumigant, nematocide, additive for antiknock fluids

Insecticioes Organic synthesis NA

Solvent, organic synthesis

Herbicides

Impurity in the herbicide 2,4,5-T

Manufacture of synthetic rubber and plastics, pharmaceuticals, insecticides, fungicioes

Insecticides Insecticides

Chemical manufacturing, anesthetic, solvent, refrigerants,

insecticides Plastics

Plasticizers
Insecticide and larvicide intermediate

Refrigerants, intermediate, blowing agent for foams

Insecticides

Degradation product of heptachlor, also acts as an

insecticide

NA

Solvent, transformer and hydraulic fluid, heat-transfer liquid

Contaminant

Examples of usesd

Hydrocarbons with specific elements (e.g., with N,P,S,CI,Br,I,F) (cont'd) a-Hexachlorocyclonexane (= Benzenehexachloride, or o-BHC) 8-Hexachlorocyclohexane (3-BHC) 7-Hexachlorocyclohexane (1-BHC or Lindane)

Hexachloroethane

Hexachloronorbornadiene Kenone Malathion Methoxychlor Methyl bromide Methyl parathion Parathion Pentachlorophenol (PCP)

Hexachlorocyclopentadiene

Phorate (Disulfoton) Polybrominated bipnenyls Polychlorinated biphenyls (PCBs) Prometon RDX (Cyclonite) -Simazine Tetrachloropenzene Tetrachloroethanes (1,1,1,2 & 1,1,2,2)

Tetrachloroethylene (or perchloroethylene, FCE) Toxaphene Triszine 1.2.4-Trichlorocenzene

Trichloroethanes (1.1,1 and 1,1,2) 1,1,2-Trichloroethylene (TCE)

Trichlorofluoromethane (Freon 11) 2.4.6-Trichlorophenol 2.4.5-Trichlorophenoxyacetic acid (2,4,5-T)

Insecticides

Insecticides

Insecticides

Intermediate for resins, dyestuffs, pesticides, fungicides, pharmaceuticals Solvent, pyrotechnics and smoke devices, explosives, organic synthesis

NA **Pesticides** Insecticides Insecticides

Fumigants, pesticides, organic synthesis

Insecticides Insecticides

Insecticides, funçicides, bactericides, algicides, herbicides,

wood preservative

Insecticides

Flame retardant for plastics, paper, and textiles Heat-exchange and insulating fluios in closed systems

Explosives Herbicides NΔ

Degreasers, paint removers, varnishes, lacquers, photographic film, organic synthesis, solvent, insecticides, fumigants, weed killer

Degreasers, crycleaning, solvent, drying agent, chemical manufacturing, heat-transfer medium, vermifuge

Insecticides Herbicides

Solvent, oyestuffs, insecticides, lubricants, heat-transfer medium (e.g., coolant)

Pesticides, degreasers, solvent

Degreasers, paints, drycleaning, dyestuffs, textiles, solvent, refrigerant and heat exchange liquid, fumigant, intermediate, aerospace operations

Solvent, refrigerants, fire extinguishers, intermediate Fungicides, herbicides, defoliant

Herbicides, deloliant

APPENDIX A ORGANICS KNOWN TO OCCUR IN GROUNDWATER - CONTINUED

Contaminant

Examples of usesa

Hydrocarbons with specific elements (e.g., with N,P,S,Cl,Br,I,F) (cont'd) 2,4,5-Trichlorochenoxypropionic acid (2,4,5-TP or Silvex) Trichlorotrifluoroethane

Trinitrotoluene (TNT

Tris-(2,3-dibromopropyl) phosphate Vinyl entoride

Other hydrocarbons
Alkyl sullonates
Cyclonexane
1,3.5,7-Cyclooctatetraene
Dicyclopentadiene (DCPD)

2.3-Dimethylhexane Fuel oil Gasoline Jet tuels Kerosene Lignin

Methylene blue activated substances (MBAs) Propane Tannin

4.6.8-Trimethyl-1-nonene Undecane Herbicides and plant growth regulator

Drycleaning, fire extinguishers, refrigerants, intermediate, drying agent Explosives, intermediate in dyestulls and photographic chemicals

Flame retardant

Organic synthesis, polyvinyl chloride and copolymers, adhesives

Detergents
Organic synthesis, solvent, oil extraction
Organic research
Intermediate for insecticides, paints and varnishes, flame retardants
NA
Fuel, heating
Fuel

Fuel, heating, solvent, insecticides

Newsprint, ceramic binder, dyestuffs, drifling fuel additive, plastics

Dyestuffs, analytical chemistry

Fuel, solvent, refrigerants, propellants, organic synthesis Chemical manufacturing, tanning, textiles, electroplating, inks, pharmaceuticals, photography, paper NA

Petroleum research, organic synthesis

Clisted uses are primarily industrial applications. Some substances occur naturally in groundwater and may not be a result of human activities.

(After OTA, 1984.)

-Sources of Groundwater Contamination

Category I—Sources designed to discharge substances Subsurface percolation (e.g., septic tanks and cesspools) Injection wells

Hazardous waste

Non-nazardous waste (e.g., brine disposal and drainage) Non-waste (e.c., enhanced recovery, antificial recharge, solution mining, and in-situ mining)

Land application

Wastewater (e.g., spray irrigation) Wastewater byproducts (e.g., sludge) Hazardous waste

Non-nazardous waste

Category II—Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release

Landfills

Industrial hazardous waste Industrial non-hazardous waste

Municipal sanitary

Open dumps, including illegal dumping (waste)

Residential (or local) disposal (waste)

Surface impoundments Hazardous waste Non-nazardous waste

Waste tailings Waste piles

Hazardous waste

Non-hazardous waste

Materials stockpiles (non-waste)

Graveyards

Animal burial

Aboveground storage tanks

Hazardous waste

Non-hazardous waste

Non-waste

Unperground storage tanks

Hazardous waste

Non-hazardous waste

Non-waste

Containers

Hazardous waste

Non-hazardous waste

Non-waste

Open burning and detonation sites

Radioactive disposal sites

Category III-Sources designed to retain substances during transport or transmission

Pipelines

Hazardous waste Non-hazardous waste

Non-waste

Materials transport and transfer operations

Hazardous waste Non-hazardous waste

Category IV—Sources discharging substances as consequence of other planned activities

Irrigation practices (e.g., return flow)

Pesticide applications Fertilizer applications Animal feeding operations De-icing salts applications

Urban runoff Percolation of atmospheric pollutants

Mining and mine orainage Surface mine-related Underground mine-related

Category V-Sources providing conduit or inducing discharge through altered flow patterns

Production wells

Oil (and gas) wells

Geothermal and heat recovery wells

Water supply wells

Other wells (non-waste)

Monitoring wells

Exploration wells

Construction excavation

Category VI—Naturally occurring sources whose discharge is created and/or exacerbated by human activity

Groundwater—surface water interactions

Natural leacning

Salt-water intrusion/brackish water upconing (or intrusion of

other poor-quality natural water)

SOURCE, Office of Technology Assessment.



APPENDIN O: GLOSSARY

- breakthrough: The appearance of a contaminant in granulated activated carbon (GAC) effluent because the contaminant is poorly adsorbed, carbon adsorption sites are filled or compound is desorbed due to competitive adsorption.
- Henry's Law Constant (atm m³/mol): Describes the relative tendency of a compound dissolved in an aqueous solution (water) to become dissolved in a gaseous solution (clean air) at equilibrium. A high Henry's constant indicates that equilibrium favors the gaseous phase. Therefore, a compound with a high constant is more easily stripped from water than one with a lower constant.
- hydrophobic: Literally "fear of water"; a hydrophobic compound is not readily dissolved in water.
- <u>in-situ</u>: In place. <u>In situ</u> groundwater treatment techniques treat water while it is in the unsaturated zone or aquifer.
- off-gas: The exit air from an aeration system that contains the volatile component which was removed (stripped) from the contaminated water.
- PCE: See tetrachloroethylene
- pilot studies: Studies that duplicate on a small scale actual specific field conditions in order to obtain equipment performance data. This information is used to design the full scale unit.
- priority pollutants: Toxic compounds listed in Appendix D 40 CFR 122 under section 307(a)(1) of the Clean Water Act.
- TCE: See trichloroethylene
- TCEa: See trichloroethane
- tetrachloroethylene (PCE): Synthetic chlorinated organic compound. This solvent is widely used in dry cleaning and metal degreasing. It is a common groundwater contaminant.
- 1,1,1 trichloroethane (TCEa): Synthetic chlorinated organic compound that has replaced TCE in many household and industrial products. Solvent in septic tank cleaners and many other products. It is a common groundwater contaminant.

APPENDIN 0: GLOSSAP1 -continued

Trichloroethylene (TCE): Synthetic chlorinated organic compound, relatively volatile. Has been used in the past as an industrial solvent, septic system cleaner and in many household products. It is one of the most common groundwater contaminants.

VOCs: See volatile organic compounds

volatile organic compounds (VOCs): A general category of synthetic organic (compounds of carbon) chemicals that generally have low molecular weights and limited solubility in water.

